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A study of the supercooling behavior of high purity liquid bismuth

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A STUDY OF THE SUPERCOOLING BEHAVIOR OF HIGH PURITY LIQUID BISMUTH

by

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ABSTRACT

This investigation involves a study of the supercooling behavior of pure bismuth as affected by the melting atmosphere, the amount of superheat, and the intentional addition of metallic and non-metallic foreign materials to the melt. It was found that the amount of oxide on the melt surface is a controlling factor in the degree of supercooling obtainable in bismuth. In the presence of a thick bismuth oxide surface layer the amount of superheat below 15°C drastically decreases the amount of supercooling due to the retention of nuclei in the surface film that promote nucleation upon cooling of the melt.

Of the 40 foreign materials intentionally added to the bismuth melt only 9 altered its supercooling behavior. These materials, in order of decreasing effectiveness in reducing the supercooling, were antimony, tellurium, selenium, indium, cadmium, lead, copper, silver and gold.

A drastic reduction in supercooling resulted by the addition of small concentrations (less than about 10 ppm) of antimony and tellurium whereas the other elements had a moderate to slight effect. Since all of these elements completely dissolved in the melt, a mechanism was

proposed whereby the elements are concentrated on the melt surface, either in elemental or oxide form, as a monolayer of atoms. This monolayer can act as a site for heterogeneous nucleation depending upon its crystallographic relationship to the (111) of bismuth. The experimental evidence presented in the investigation lends support to the disregistry theory proposed by Turnbull and Vonnegut.

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I. INTRODUCTION

The field of heterogeneous nucleation is of extreme importance in the solidification of most metals and alloys. Many important metallurgical processes require that this type of nucleation be controlled so that improved properties and characteristics are obtained for a particular component. For example, the process of inoculating liquid cast iron with a magnesium alloy addition promotes nucleation of spheroidal graphite instead of flake graphite normally obtained in gray iron. The process whereby the grain size of a casting is reduced by promoting nucleation through alloying additions known as grain refiners is another application of controlled heterogeneous nucleation. Although the results of heterogeneous nucleation have been known for many years the actual mechanism is not completely known.

The present investigation was established to study the phenomena of heterogeneous nucleation through supercooling measurements in high purity bismuth. Bismuth was selected since it can be readily supercooled in large samples and there are very few materials that promote the nucleation of bismuth. Large amounts of supercooling are desired in the melt to give a greater latitude in which

to study heterogeneous nucleation. Thus, by intentionally adding foreign materials to the melt and observing the charge in supercooling, if any, one can determine the effectiveness of a particular nucleating agent. Knowledge of the degree of effectiveness of these nucleating agents may thus lead to a better understanding of nucleation behavior which can be directly applied to actual metallurgical processes.

II. LITERATURE REVIEW

The present investigation involves a study of some of the factors that affect the degree of supercooling of high-purity liquid bismuth. This type of a study can be classified as nucleation phenomena occuring during the liquid-solid transformation. This review will thus be restricted to nucleation in liquid-solid transformations except where it will be necessary to include some discussion of nucleation occuring during the vapor-liquid transformation since the general nucleation theory was originated on this type of transformation.

The literature review will also be restricted to the study of metallic systems, however, some non-metallic systems will be included due to their importance to the study of nucleation phenomena and their relation to the present investigation.

The review of literature on nucleation will be divided into two main sections, namely, theoretical studies and experimental studies. The latter section will be divided into nucleation experiments using liquid droplets and nucleation experiments in bulk liquids. For this classification, a liquid droplet indicates a somewhat spherical

geometry where each droplet has a diameter less than a few millimeters. A bulk liquid thus implies any size greater than this but in most cases means a melt having a fairly large continuous mass. This rough distinction is only made to group the type of experiments that have been performed into an organized system.

(A) Nucleation-Theoretical Studies

Nucleation phenomena can be classified as either homogeneous or heterogeneous. Homogeneous nucleation is spontaneous nucleation occurring without the aid of a foreign surface while heterogeneous nucleation requires the aid of a foreign surface to promote nucleation. The basic theory of homogeneous nucleation was originated by the work of Volmer and Weber(1) and Becker and Doring(2). The Volmer and Weber theory was developed for the homogeneous nucleation of a liquid phase from a supersaturated vapor phase. They assumed that clusters of molecules exist in equilibrium with the vapor phase and that these clusters, called "embryos", can grow or disappear back into the vapor phase depending upon their surface and volume energies. They derived an expression for the total free energy of the system that includes a surface energy term and volume energy term as follows:

$$\Delta F = 4\pi r^2 \sigma + \frac{4}{3}\pi r^3 \Delta F_v \qquad (1)$$

Where:

ΔF = Total free energy change of the system.

σ = Surface energy between the liquid and Vapor phases.

ΔF_v = Volume free energy between the liquid and vapor phases.

r = Radius of the cluster of molecules.

This equation was derived assuming a spherical geometry of the cluster. Since the surface energy term is always positive and the volume energy term is always negative, the total free energy of the system vs. the radius of the cluster can be plotted as shown in figure 1. As can be seen, the free energy curve reaches a maximum at ΔF^* and r^* where ΔF^* represents the free energy required to form a cluster of molecules of critical radius, r^*. A cluster having a radius of r^* can either grow into a stable nucleus by the addition of more molecules or it can diminish in size by losing some of its molecules. The only way a stable nucleus can form is by attaining the energy ΔF^* which is called the "free energy of nucleation".

The maximum value of free energy can be derived by differentiating equation (1) with respect to r and setting it equal to zero. Thus:

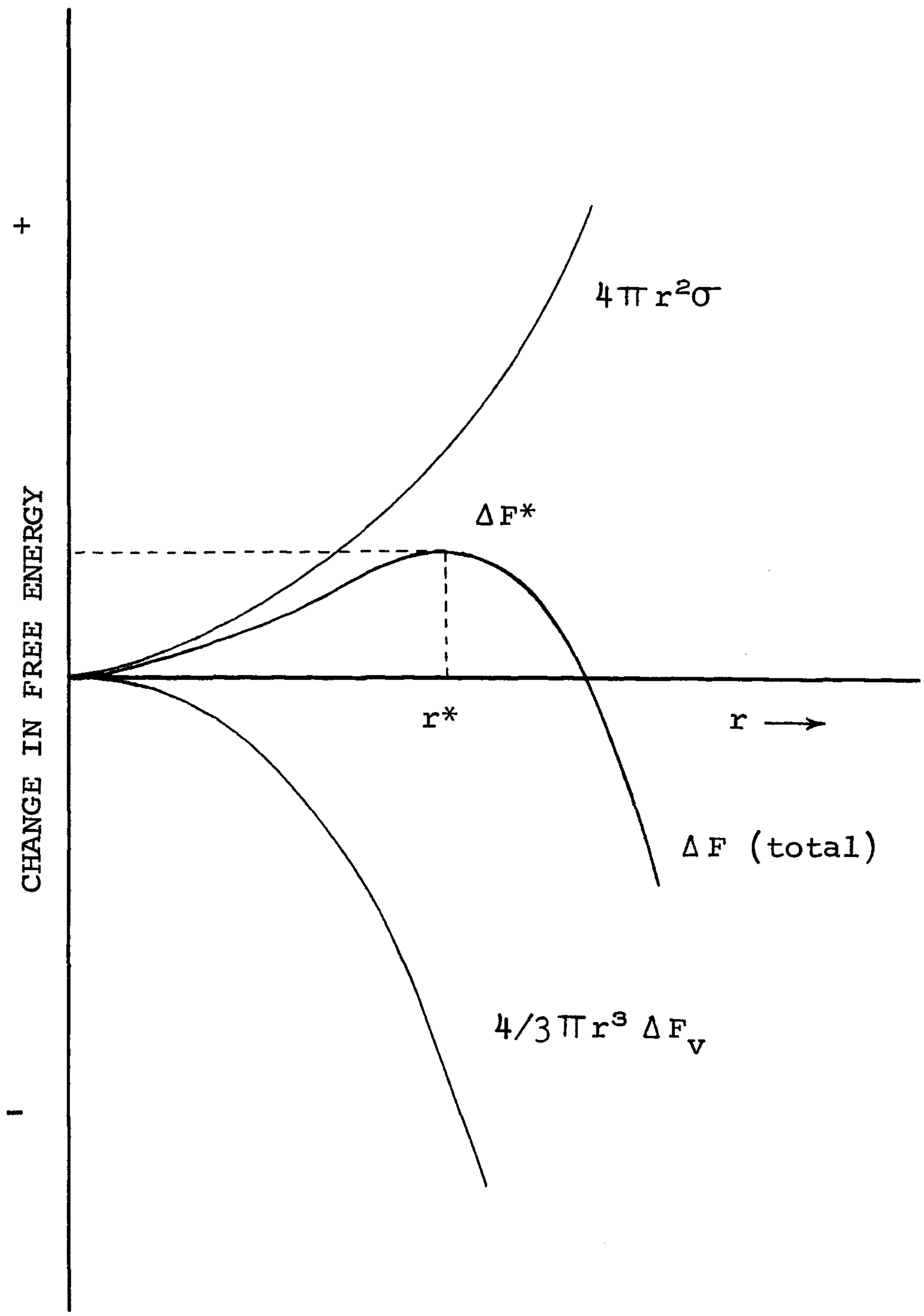


Figure 1

A Plot of Change in Free Energy vs. The

Radius of A Spherical Cluster

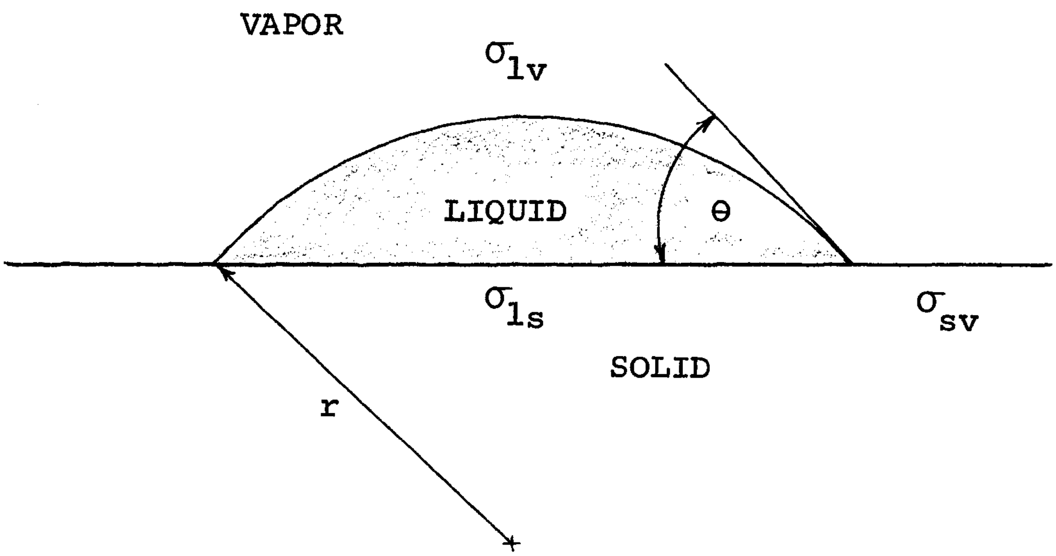
$$\Delta F^* = \frac{16\pi\sigma^3}{3\,\Delta F_V^2} \tag{2}$$

and the radius of the critical cluster is:

$$r^* = \frac{-2\sigma}{\Delta F_V} \tag{3}$$

A few years later, Becker and Doring(2) modified the proposed treatment of Volmer and Weber by considering that the number of embryos that exist in equilibrium with the vapor phase are decreased by the rapid growth of certain stable nuclei into macroscopic droplets. Thus, the accepted theory of homogeneous nucleation is based on these two treatments.

Volmer(3) using the basic assumption of the Volmer and Weber theory for homogeneous nucleation developed a formal theory for heterogeneous nucleation. This theory was developed for a liquid cluster to condense or nucleate on a foreign surface from a supersaturated vapor. When the embryo comes to equilibrium on a flat foreign surface it forms a spherical cap with a certain contact angle, θ, as shown in figure 2. This relationship takes into account the interfacial energies between the liquid on the surface and the vapor and the surface. The equation



Where:

$$\sigma_{sv} - \sigma_{ls} = \sigma_{lv} \cos \theta$$

Figure 2

Interfacial Energy Relationships for Heterogeneous Nucleation of A Liquid From The Vapor Phase

proposed by Young[4] in 1805 was used to relate these interfacial energies as follows:

$$\cos \theta = \frac{\sigma_{SV} - \sigma_{LS}}{\sigma_{LV}} \tag{4}$$

Where:

θ = Contact angle between the spherical cap and the foreign surface.

σ_{SV} = Interfacial energy between the vapor and the solid.

σ_{LS} = Interfacial energy between the liquid and the solid.

σ_{LV} = Interfacial energy between the vapor and the liquid.

Volmer modified the proposed equation for homogeneous nucleation theory to include a contact angle function, $f(\theta)$. Thus:

$$\Delta F^* = \frac{16 \pi \sigma^3}{3 \Delta F_V^2} f(\theta) \tag{5}$$

Where:

$$f(\theta) = \frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \tag{6}$$

The contact angle function, $f(\theta)$, varies from 0 to 1 as the contact angle varies from 0° to 180°. At a contact angle of 180° the cluster does not come in contact with the surface and nucleation is essentially homogeneous

($f(\theta) = 1$). When the contact angle is 0° complete "wetting" occurs ($f(\theta) = 0$) and the free energy of nucleation is zero. This indicates that for any contact angle between 0° and 180° heterogeneous nucleation occurs and the free energy of nucleation, ΔF^*, is less than that required for homogeneous nucleation.

The above equations hold for vapor-liquid, liquid-solid and solid-solid transformations. Since the present investigation involves a liquid-solid transformation, the equations will be used in this describing nucleation in a metallic melt.

Hollomon and Turnbull(5) have modified the expression for ΔF^* in equation (5) to include terms characteristic of the liquid-solid transformation as follows:

$$\Delta F^* = \frac{16\pi T_M^2 \sigma_{SL}^3}{3\Delta H_f^2 (\Delta T)^2} f(\theta) \qquad (7)$$

Where:

T_M = Melting temperature.

σ_{SL} = Solid-liquid interfacial energy.

ΔH_f = Latent heat of fusion.

ΔT = Supercooling.

This expression places the free energy of nucleation in terms of measurable quantities.

Vulmer[6] later proposed that the surface required for heterogeneous nucleation is not flat but contains microcavities. These microcavities can retain stable clusters of the nucleated phase above the equilibrium melting temperature, T_M, where they would not normally exist. This theory was proposed to explain the thermal history phenomena observed in many metallic and non-metallic systems. Thus, if these stable clusters were not destroyed by excessive superheating (the difference in temperature of the liquid above T_M and T_M), they would promote further nucleation and growth during freezing and small amounts of supercooling (the difference in temperature of the liquid below T_M and T_M) would be obtained. If the retained clusters were destroyed, a greater amount of supercooling should be obtained and the usual heterogeneous nucleation relationships would be obeyed. Turnbull[7] later applied this theory to a number of metallic systems assuming cylindrical microcavities in the catalytic surface. Turnbull calculated that, for a particular contact angle, the amount of supercooling should increase as the amount of superheating is increased until a limiting value is obtained when the stable clusters are destroyed in the liquid. Turnbull calculated this relationship for the metal gallium which has a pronounced

thermal history effect. For example, gallium at a superheat of 5°C could have an embryo of about 140 A° in diameter retained in a cylindrical microcavity and this embryo is capable of growing at a supercooling of about 9°C. If the superheat is increased to 20°C the maximum diameter of a retained embryo is about 34Å and a resulting supercooling of about 34°C is obtainable. The calculated values are similar to those observed in bulk samples of liquid gallium.

Turnbull and Vonnegut[8] have proposed a mechanism to explain nucleation catalysis (heterogeneous nucleation) in the liquid-solid transformation. They have proposed that the degree of potency of a catalytic substrate to promote nucleation is dependent upon the boundary coherency between the nucleated solid and the substrate. The boundary coherency is related to the degree of misfit or disregistry between the lattice parameters of the nucleated solid and the substrate. The degree of potency then varies with the reciprocal of the disregistry of the low index planes of the substrate and the solid. The amount of supercooling of a liquid is a function of the disregistry factor squared and decreases as the disregistry factor decreases.

(B) Nucleation-Experimental Studies

(1) Nucleation Experiments Using Liquid Droplets

The nucleation behavior of metallic melts was studied as early as 1845 by Levol[9]. Levol observed that gold droplets, formed during fire assaying, could be supercooled below their melting temperature. The solidification of the droplets exhibited a sudden flash of light or "luminescence" effect which was attributed to a reaction of the dissolved oxygen with impurities in the droplets. This same phenomena was reported later by Von Riemsdijk[10] who attributed the sudden brightening to the rapid release of the heat of fusion of the gold. In 1908, Mendenhall and Ingersoll[11] made a systematic study of this phenomena in liquid droplets of gold, platinum, palladium, rhodium, iridium, and silicon. The droplets ranged in size from 50 to 100 microns in diameter. These investigators observed that the smaller the droplet and the higher its melting temperature the greater the degree of supercooling obtained. As an example, small droplets of both platinum and rhodium could be supercooled as much as 370°C. They also observed that the greater the degree of supercooling the greater the intensity of the sudden brightening during solidification.

More recently Vonnegut[12], using a special dilatometer technique, studied the rate of solidification in a dispersion of tin droplets between 1 and 10 microns in diameter. Supercooling as much as 110°C was observed in these tin droplet dispersions. The droplets were coated with an oxide film to prevent coalescing. A large number of droplets were used in these dispersions in order to isolate the effective nucleation catalyst particles in a small number of droplets thus allowing the majority of the droplets to solidify at a large degree of supercooling.

Turnbull[13] using a similar technique studied the supercooling of dispersions of small droplets of mercury, bismuth, gallium and lead. The droplets were coated with oxide, oleate and iodide films. He observed that the dispersions could be supercooled to between 0.75 and 0.87 of their absolute melting temperatures before solidification occurred.

Wang and Smith[14] studied the supercooling behavior of copper alloyed with lead or bismuth and aluminum alloyed with 10% tin. These systems were selected since they freeze as eutectic alloys with the primary phase freezing out at a temperature close to the freezing temperature of the pure component. On cooling of these alloys the primary phase

does not change in composition and the secondary phase is dispersed as isolated liquid droplets at a temperature near the eutectic temperature. In the aluminum -10% tin alloy the dispersed tin (secondary phase) droplets supercooled between 99°C and 130°C.

Turnbull and Cech[14] using a hot-stage microscope observed the solidification of a number of small droplets of 10 to 100 microns in diameter. They obtained supercooling data for selenium, bismuth, lead, antimony, aluminum, germanium, silver, gold, copper, manganese, nickel, cobalt, iron, and palladium using vacuum and hydrogen or helium atmospheres. They found that most of the metals obtained a maximum supercooling of about 0.18 times the absolute melting temperature.

Turnbull[16], using a dilatometric technique, studied the effect of various coatings on the supercooling of dispersions of mercury droplets ranging from 2 to 400 microns in diameter. The coatings consisted of mercury sulfide, oleate, iodide, acetate, stearate, laurate, benzoate and oxide. He found the solidification rate of the supercooled mercury droplets to be strongly dependent upon the type of coating used. The mercury droplets coated with mercury laurate gave the highest supercooling (70°C) which indicated

that the droplets were homogeneously nucleated. Droplets with the other coating materials were supercooled to a less degree indicating a heterogeneous nucleation phenomenon.

Cech and Turnbull[17] investigated the supercooling behavior of copper-nickel alloy droplets 30 to 50 microns in diameter. They found that the maximum supercooling obtainable is about 0.18 times the absolute liquidus temperature for the particular alloy droplet. This is in close agreement with previous studies on pure metals.

Hollomon and Turnbull[18] studied the solidification of lead-tin alloy droplets 30 to 50 microns in diameter. A total of 12 alloy compositions were investigated ranging from 5 atomic percent to 90 atomic percent lead. They found that, in this eutectic system, the temperature of nucleation is higher for all the alloy droplets than for the pure components. They also found that the lead-rich crystalline phase had a mild catalytic effect on the nucleation of the tin-rich solid solution but that the reverse effect was not observed.

Pound and LaMer[19] using the dilatometric technique studied the supercooling behavior of oxide coated tin droplets of about 5 microns in diameter. A dispersion of about 10^{10} droplets was employed and the resulting supercooling

was about 10° lower than that previously determined. This indicated that a material of higher purity was used for this investigation. They also measured the rate of nucleation and found that the rate increases rapidly with a decrease in temperature and increase in droplet size.

Vonnegut[20] performed an interesting experiment involved with the nucleation behavior of a supercooled fog (water) in the presence of suspended silver iodide crystals. Silver iodide was found to be the most potent catalyst for the formation of ice crystals in a supercooled fog or cloud. Vonnegut related the close fit between the lattice parameter of silver iodide and ice to the degree of potency of the catalyst. Using silver iodide crystals a maximum supercooling of only 2.5°C was obtainable. Schaefer[21] also studied this behavior using naturally occurring inorganic substances like volcanic ash, clay, etc. The substances were not as potent in causing nucleation as silver iodide and could not be related, due to the complexity of their structure, to the lattice misfit effect. The supercoolings ranged from 11°C to 23°C depending on the material.

Bradshaw, Gasper and Pearson[22] recently studied the nucleation behavior of gold droplets, 60 to 200 microns in diameter, with the addition of intentional catalysts. A

hot-stage microscope was used to observe the supercooling under a variety of atmospheres. The catalysts added to the gold droplets consisted of powdered zinc oxide, alumina, magnesia, mica, graphite, diamond, tungsten carbide, zirconium carbide, titanium carbide and titanium nitride. These investigators found the carbides and nitrides to be the most effective nucleation catalysts. They found that the lattice misfit was not the significant factor in nucleation. The effect of the atmosphere on the nucleation behavior was observed when droplets melted in argon or hydrogen indicated no marked supercooling behavior while gold droplets melted in air or oxygen had mean supercoolings of 129°C, 97°C, and 159°C respectively. They concluded that the foreign catalysts that were present were oxidized thus rendering them ineffective in promoting nucleation.

Sundquist and Mondolfo[23][24] more recently studied the nucleation behavior of 60 binary alloy systems using a hot-stage microscope. The alloy droplets, ranging from 100 to 300 microns in diameter, were melted either in a high vacuum or a hydrogen atmosphere. The freezing temperature was observed by the sudden change in the surface features of the droplets. They concluded that metals that are good nucleating agents are difficult to nucleate and

vice versa. The metals that are good nucleating agents have an "open" or complex crystal structure (bismuth antimony, etc.) and have high entropies of fusion and high solid-liquid interfacial energies. Similarly, metals with simple structures (lead, thallium, gold, etc.) are easy to nucleate and have low entropies of fusion and low interfacial energies. In all of the binary systems studied, one phase would be more effective in nucleating the other than vice versa. They found that the lattice misfit effect was not a controlling factor in heterogeneous nucleation. They also found that bismuth could not be nucleated by any of the nucleating agents studied in the investigation.

(B) Nucleation Experiments in Bulk Liquids

Webster[25] in 1933 studied the supercooling behavior of bismuth, cadmium, lead and tin. The metals were melted in quartz crucibles that were open to the atmosphere. Webster found that there is a definite correlation between the amount of supercooling and the amount of superheat for a given melt. The amount of supercooling increases as the amount of superheat increases until a limiting value is reached where the supercooling remains constant for any given superheat. This limiting value of supercooling

was found to be between 30° to 35°C for bismuth, about 3°C for lead, and between 20° to 25°C for tin. Cadmium melts exhibited no appreciable supercooling at any given superheat.

In the late 1940's and early 1950's considerable interest was generated in the field of grain refinement of cast structures. This phenomenon involves a study of the effect of intentional addition of foreign elements or catalysts on the nucleation behavior of bulk liquid melts. Eboral(26) studied the effect of small additions of titanium, vanadium, zirconium, molybdenum, chromium, niobium, boron and tungsten on the final grain size of sand cast aluminum. He found that all the elements except chromium produced a fine equiaxed grain structure in the cast samples.

Ruddle(27) observed that considerable supercooling could be obtained in castings of super-pure aluminum and aluminum-copper alloys. When small amounts of titanium were added to the melt the supercooling was drastically decreased. The addition of titanium also produced a fine equiaxed grain size in the castings.

Cibula(28)(29) investigated the effect of various alloying additions on the supercooling behavior and final grain

size of pure aluminum castings. He found that large amounts of copper and nickel when added to pure aluminum did not have a marked effect on the supercooling behavior. Very small additions of certain elements such as titanium, vanadium, boron, niobium, and zirconium produced a fine equiaxed grain size with no evidence of supercooling. Cibula concluded that grain refining nuclei were formed by the addition of these latter elements to pure aluminum. These grain refining nuclei were identified as carbides. These carbides (titanium carbide) contain atoms of carbon in interstitial position in a simple metallic lattice whose dimensions are similar to those of the aluminum lattice.

Reynolds and Tottle[30] investigated the nucleation behavior of zinc, aluminum, magnesium, tin, lead, copper and antimony castings by applying metal powders to the mold face of a standard dry-sand mold or metallic mold. The effects of these elements as nucleation agents was observed by comparing the final grain size of the casting surface exposed to the powders to the unexposed surface. They found that the metal powders that had a similar crystal structure to that of the melt material were effective nucleating agents if the lattice "misfit" was within 10%. If the lattice misfit was greater than 10% no positive results were obtained.

The inoculation and grain growth inhibitation effect of various substances on the grain refinement of copper was recently investigated by Gould, Form and Wallace[31]. Various intermetallic compounds and pure metals were added to melts of pure copper and the effect of these materials on the final grain size and shape of the solidified structure was observed. It was found that the intermetallic compounds did not alter the final grain size from that of the pure copper ingot. Cobalt, iron and tungsten powders decreased the grain size and changed the cast structure from columnar to equiaxed. These three elements have a similar lattice parameter to that of pure copper. Bismuth and lithium additions not having a low disregistry factor, also produced an equiaxed structure. Lead, calcium, magnesium, tin, selenium, and tellurium did not alter the final grain structure of pure copper.

Danilov and Ovsienko[32] have studied the effect of vacuum and an air atmosphere on the supercooling behavior of pure bismuth. When melted in air the bismuth supercooled to a maximum of 12° to 13°C and when melted in a vacuum a maximum supercooling of 45° to 46° was obtained. In the vacuum the supercooling is practically independent of the superheat. They concluded that the bismuth oxide is an active substance in promoting nucleation.

Bosio, Defrain and Epelbain[33] investigated the supercooling behavior of pure bismuth melts 0.02 to 8 grams in mass. They melted the bismuth in air and also under a flux consisting of 64% stannous chloride, 18% zinc chloride and 18% thallium chloride. By melting a 5 gram sample in air these authors found the existence of a linear correlation between superheat and supercooling below a limiting value of 10°C superheat. Above this limiting value a fairly constant value of 30°C supercooling is obtained. By using the ternary flux, they obtained supercoolings as high as 121°C in both small melts (0.02 g) and large melts (8 g). These investigators also studied the effect of small additions of other metals on the supercooling of bismuth. They found that copper decreases the degree of supercooling while silver, manganese, lead, platinum, antimony, silicon, and tin have no effect.

Childs[34] has obtained a supercooling value approaching 90°C in bulk melts of high purity bismuth. He found that by employing an anhydrous tin chloride flux on the surface of the liquid bismuth any oxide that may be present is dissolved in the flux.

Glicksman and Childs[35] investigated the effect of catalytic substrates on the supercooling of liquid tin.

The tin was melted in a Pyrex crucible in a vacuum of 10^{-5} torr. The substrate was brought into contact with the liquid tin by means of a moveable vertical shaft and the supercooling was measured by a glass encapsulated thermocouple immersed in the melt. The supercooling was measured with and without the presence of the substrate and the change in supercooling, if any, was recorded. The substrates used were Sn, Pt, Y, Ag, Al, TiC, MoS, SiC, Al_2O_3, CeS, MgO and graphite in single crystal and polycrystalline form. They obtained reproducible results with the Pt, Y, Ag, TiC, MoS and Al substrates by changing the background supercooling of about 38°C to 4°, 6°, 7°, 15°, 17°, 18°C respectively. The other substrates did not give characteristic results. The yttrium single crystal gave 2 characteristic supercooling values depending on the crystallographic plane exposed to the melt. This element has a similar lattice spacing to that of tin. The authors found that the metallic substrates were more potent as nucleating agents than the non-metallic materials. The aluminum catalyst gave a higher supercooling than was expected due to the adherent insoluble aluminum oxide film that prevented proper substrate to melt contact.

Jubb[36] studied oxidation and deoxidation of bulk samples of zone-refined tin. Deoxidation of the tin melt was done by melting in a vacuum of 10^{-5} torr at 950°C for a period of two hours. The deoxidized tin supercooled to a maximum value of 6°C. Upon oxidizing the deoxidized tin in dry air then evacuating the system, the supercooling could be increased to 25° to 33°C. Jubb also found that graphite, carbon and silica are excellent nucleating catalysts for liquid tin in the absence of the tin oxide surface phase. He found that by dissolving aluminum in the molten tin the supercooling could be changed from 40°C to 5 to 8°C indicating that aluminum is also an excellent nucleation catalyst in the absence of the tin oxide surphase.

Mannchen and Puttrich[37] studied the effect of small additions of carbon, silicon and germanium on the supercooling of 50-gram melts of pure antimony under hydrogen or argon atmospheres. Using an argon atmosphere they obtained an average supercooling of about 45°C and by adding a very small quantity of carbon (2.5 mg) the supercooling was reduced to about 6°C, Silicon (6.8 mg) reduced the supercooling to about 13°C and germanium (6.1 mg) to about 6°C. By melting in a hydrogen atmosphere slightly higher

values of supercooling were obtained. The investigators also studied the effect of gamma-radiation on the supercooling behavior in the presence of the above elements. They concluded that the radiation produced various ionization potentials of the elements and the supercooling was dependent upon the ionization potential of the effective impurities.

Very recently Davis and Fryzuk[38] studied the effect of the degree of supercooling on the grain structure and solute distribution of 40 gram samples of pure bismuth and a 100 ppm silver-bismuth alloy. For the alloy, Ag^{110} was used to serve as a tracer and a solute in the bismuth. The bismuth was melted, under a flux of tin, zinc and thallium chlorides. This ternary flux was selected so that a large degree of initial supercooling could be obtained. The amount of supercooling obtained was regulated by inserting a cold silica rod into the melt. At small degrees of supercooling a large number of nuclei are formed in the melt resulting in a small grain size in the solidified sample. As the supercooling is increased the resulting grain size increases since fewer nuclei have time to form. At fairly large supercoolings a subgrain structure was observed by using an autoradiographic technique.

III. EXPERIMENTAL PROCEDURE

(A) The Description of Apparatus.

The apparatus used in this investigation is shown in Figure 3 and can be divided into 4 discreet units:

(1) The Melting Furnace

(2) The Temperature Measuring System

(3) The Vacuum System

(4) The Controlled Atmosphere System

Each unit will be discussed in detail below.

(1) The Melting Furnace

The melting furnace was designed to facilitate either induction or resistance heating in a vacuum or a controlled atmosphere. The furnace allows one to perform certain manipulations under a vacuum or controlled atmosphere without introducing air into the system.

Figure 4 shows a close-up view of the melting furnace. The furnace cover and the bottom manifold sections were originally designed and built at the Argonne National Laboratory. Certain modifications have been made on the original Argonne design of the furnace cover so that the furnace could be used for nucleation experiments. Both the furnace cover and the manifold sections are made of

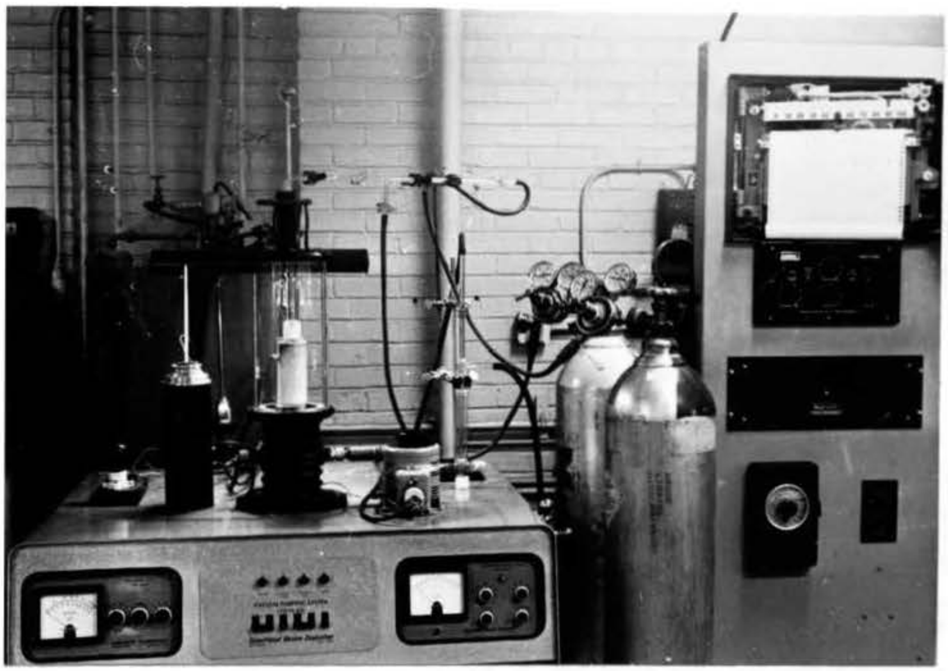


Figure 3

A General View of Experimental Apparatus

Figure 4

A Close-Up View of Melting Furnace

stainless steel and are water-cooled. The exterior portion of the furnace, between the cover and the manifold, is the furnace housing and consists of a 6" diameter 12" long heavy-walled Pyrex cylinder which permits visual observation of the melting operation. Silicone rubber compression gaskets were used between the housing and the manifold and furnace cover.

A view of the furnace cover and accessories can be seen in Figure 5. This is a view of the bottom of the cover showing the location of the 3 main ports and attachments. The central port was used for the glass-encapsulated thermocouple which was free to move in the vertical direction plus rotation. This movement can be performed under vacuum or special atmosphere, without the introduction of air into the system, since rubber vacuum seals are located inside the port opening. This is an important feature of this melting furnace since the thermocouple tube is used to stir the melt when alloying additions are made. The thermocouple tube can also be placed in the melt at a certain depth and can be removed from the melt when a particular experiment is concluded.

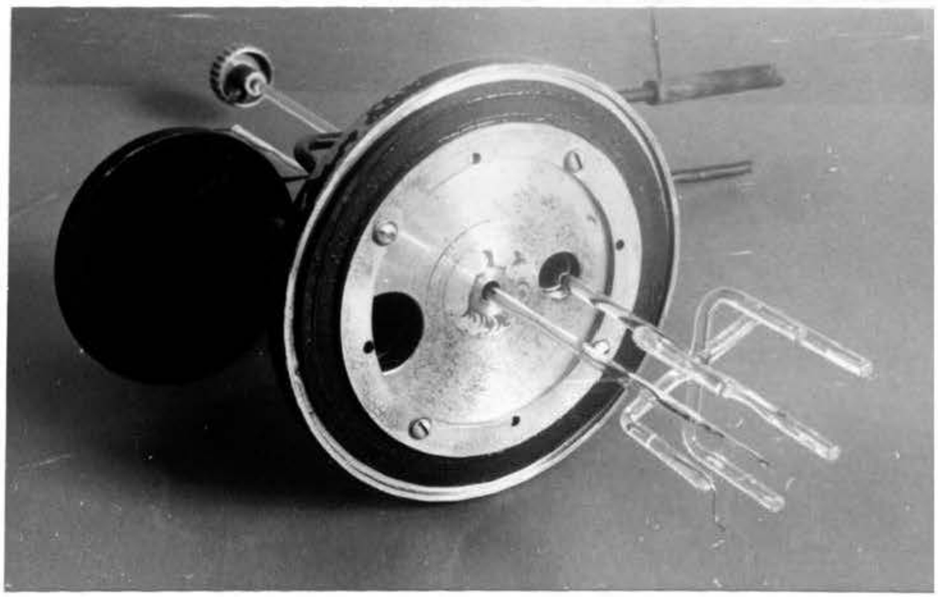


Figure 5

A View of Furnace Cover and Accessories

The right port was used for the catalyst support rod. This glass (Pyrex) rod has freedom of movement similar to the thermocouple tube. This movement is necessary so that a solid material attached to the end of the rod can be introduced into the melt and removed at any time during the experiment. Rubber vacuum seals similar to those used for the central port are necessary for this type of movement. A catalyst support rod containing as many as 6 prongs has been utilized so that different materials can be studied in the same experimental cycle. Rotation of the catalyst support rod is necessary so that the individual materials can be introduced into the melt and withdrawn in proper sequence.

The left port was used for the controlled atmosphere inlet tube. The inlet tube was designed so that the entering stream of gas was directed toward the melt. Thus, when a reducing atmosphere such as hydrogen was used, the fresh gas stream impinges directly upon the melt surface.

Figure 6 shows the manifold section and the internal portions of the furnace. The manifold section supports the furnace housing and also the internal portions of the furnace. The manifold also contains 2 ports, one of which provides an inlet for the power leads of the internal

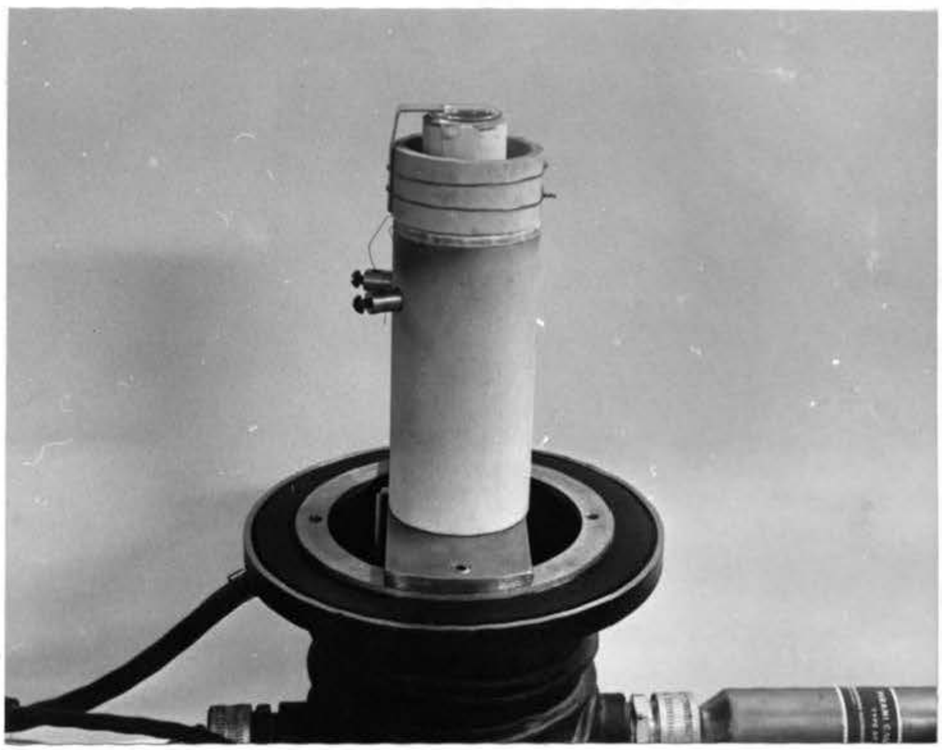


Figure 6

A View of Manifold Section

Showing The Internal Portions of The Furnace

resistance furnace and the other port houses a hot-filament ionization gauge tube. The large manifold flange rests upon the inlet flange of the vacuum system and an "o" ring type vacuum seal is used between two flanges.

The internal portion of the melting furnace as seen in the above figure can best be illustrated by the cross-sectional view of the furnace in Figure 7. The melting portion of the furnace rests upon a copper base that is attached to the manifold section. A 2" diameter 5" long Alundum cylinder with a 1/8" wall thickness was positioned on the copper base by means of a 1 3/4" diameter steel disk. This steel disk locates the Alundum cylinder in the center of the furnace housing. A 2" diameter Alundum disk rests on the top of the cylinder and provides a flat insulated surface for the resistance furnace. A 10 ml Pyrex crucible was used to contain the melt within the resistance furnace.

A 2" diameter, 1 1/2" long Alundum heat shield was used around the resistance furnace to prevent overheating of the Pyrex furnace housing. A catalyst support platform made of aluminum sheet was attached to this Alundum shield, so that a number of small alloying additions can be added

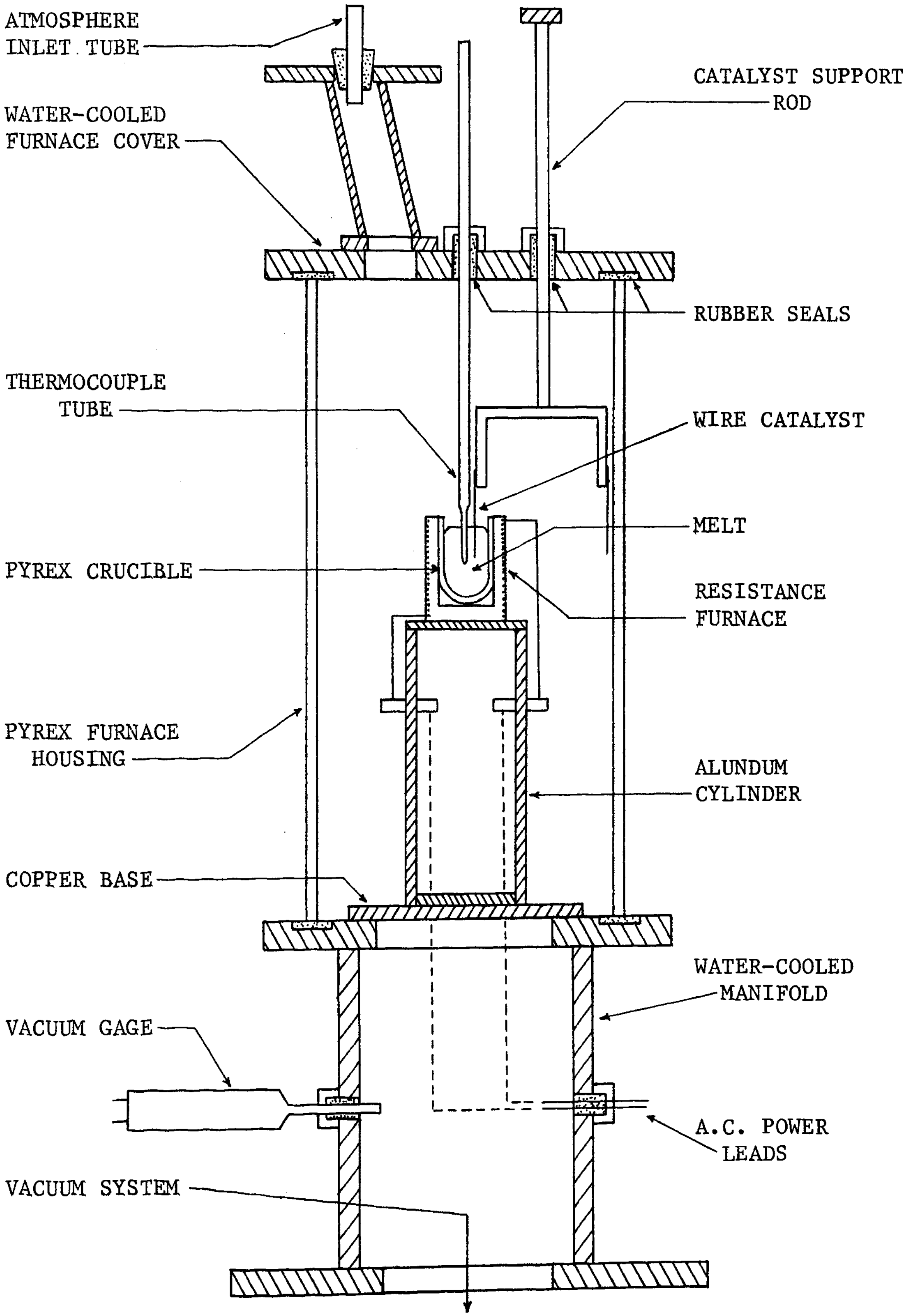


Figure 7. Cross-Sectional View of Melting Furnace

to the melt. These small additions are individually pushed off the platform into the melt by proper movement of the catalyst support rod.

It was found that resistance heating was preferable to induction heating since induced currents were generated in the thermocouple from the induction coil, thus introducing an error in temperature measurement. The resistance furnace consists essentially of 31 turns of 29 gauge Nichrome wire (5.14 ohms/foot) wound around an externally threaded Lava (American Lava Company - hydrous aluminum silicate) body. The Lava body was machined, threaded and then fired at 1900°F for 1 hour and furnace cooled. The firing operation was necessary to remove the water of crystallization and to harden the material. After winding with the Nichrome wire, the furnace was then coated with a ceramic slurry (zircon flour + aqueous colloidal silica) to protect the wire from oxidation and prevent unwinding of the coil. The furnace was then heated under vacuum to outgas any volatile material that may have been absorbed. A view of the resistance furnace, crucible with bismuth charge and glass encapsulated thermocouple is shown in Figure 8.

The electrical power to the furnace was regulated by means of a variable transformer which could vary the voltage

Figure 8

A View of Crucible with Bismuth Charge,

Thermocouple, and Resistance Furnace

from 0 to 120 volts A.C. Normal furnace voltage was maintained at 100 volts during melting. A higher voltage decreased the life of the Nichrome wire wound furnace.

(2) The Temperature Measuring System

A copper-constantan thermocouple was used to measure the temperature of the melt. The thermocouple was constructed from 28 gauge wire with an electrically-welded bead for both the hot-junction and reference junction. The reference junction of the thermocouple circuit was maintained at 0°C by immersing a bead in a distilled-water-ice mixture. A 500 cc Dewar flask was used to contain this mixture and maintain the reference temperature for at least a 48 hour period.

The temperature measuring instrument was a Honeywell Electronik strip-chart recorder with a chart speed of 8"/hr. The 5 ohm automatic reference junction compensating resistor was by-passed with a 5 ohm precision resistor so that the 0°C reference junction could be employed.

The hot-junction thermocouple bead was encapsulated in Pyrex glass. This encapsulation was used so that the metallic thermocouple wires would not affect the solidification of the melt. The encapsulation was produced by inserting the bead of the thermocouple into a molten droplet

of glass formed at the end of a 4 mm diameter Pyrex tube 18" in length. A very thin glass coating was formed around the bead as shown in the previous figure. This method was advantageous since the movement of the Pyrex tube can be controlled from outside the furnace and the Pyrex tube adds structural strength to the thermocouple proper. Other methods were initially employed using small bore capillary tubing to encapsulate the bead, but the tubing was very fragile and the movement could not be directly controlled from outside the furnace. The latter method had an additional problem in that the gap between the capillary tubing and the thermocouple bead was enough to cause a gross error in temperature measurement in a vacuum.

(3) The Vacuum System

The vacuum system located directly below the melting furnace was a type PS-40A packaged pumping system manufactured by the Consolidated Vacuum Corporation. This system consisted of a 4" oil-diffusion pump coupled with a Welch Duo-Seal mechanical pump capable of pumping at the rate of 5 cubic feet per minute. The pressure in the melting furnace could be reduced to between 10^{-5} and 10^{-6} Torr within one hour under normal operating conditions.

The mechanical pump was removed from the main chassis of the pumping system and connected to the diffusion pump by means of a 2" diameter 2' long rubber vacuum hose to eliminate the mechanical vibration caused by the pump. The chassis of the entire system was shock mounted to eliminate vibrations from the surroundings.

Two vacuum gauges were used in the system. A Pirani Vacuum gauge was used within the pressure of limits 10^{-3} and 2 Torr and a hot-filament ionization gauge was used for pressures of below 10^{-3} Torr. The Pirani gauge contains a leak detector circuit that could be used to detect rough leaks in the system. A filament protection and alarm circuit was installed in the ionization gauge circuit to protect the filament of the ionization tube from oxidation at excessive pressures.

(4) The Controlled Atmosphere System

A controlled atmosphere may be introduced into the melting furnace through the inlet tube located in the furnace cover. One or more gases can be flushed through the furnace through the inlet tube. The only gases other than air used in this investigation were pure argon and pure hydrogen.

The flow of the gas through the furnace was indicated by means of a bubble tube located at the exhaust end of the system. The exhaust gases were expelled through a tube extending to the outside of the building.

(B) <u>The Calibration of The Temperature Measuring System</u>

The thermocouple was calibrated by measuring the freezing points of indium (99.99%) tin (99.9999^{+}%) bismuth (99.9999^{+}%) and lead (99.9999^{+}%). Each metal was melted under vacuum in a 10 ml Pyrex crucible and allowed to freeze in the presence of the thermocouple immersed 4 mm in the liquid metal. Several melting and freezing cycles were run in order to get an average value of the freezing points. The freezing arrests were recorded on the strip-chart paper (relative scale from 0 to 100) for each metal listed above and the strip-chart paper was then calibrated for the particular thermocouple used. The zero point was checked by placing both the hot-junction and the reference junction in the distilled water-ice mixture. Thus 5 points have been used to determine the calibration of the strip-chart paper.

Certain calibration points were made under argon and hydrogen atmospheres to compare with those measured in vacuum and no significant differences were detected.

The same glass encapsulated thermocouple described in a previous section was used throughout the calibration procedure.

(C) <u>The Preparation of The Melt Material</u>

High-purity bismuth (99.9999+%) was used in this investigation as a host material for nucleation studies. The bismuth was purchased from the Leytess Metal and Chemical Corporation as 1/2" diameter bars 9" long. The nominal analysis is given in Table I.

A mass of about 50 to 60 grams was normally used for a melting charge. The bismuth bars were crushed in a heavy canvas cloth by means of a wooden mallet. This procedure was used to protect the high-purity material from contamination that might have resulted from mechanical cutting methods. The crushed pieces of bismuth were rough weighed on a Fisher pan-balance to produce a charge weight within the above limits.

A 10 ml round bottom Pyrex beaker was used as a crucible to contain the charge. The crucible was washed with distilled water and dried with a clean, lint-free cloth before receiving the charge. If the crucible had been used for a previous melt it was cleaned in concentrated nitric acid for 5 minutes to remove all traces of impurities.

TABLE 1

TYPICAL ANALYSIS OF HIGH-PURITY BISMUTH

Bismuth - Minimum 99.9999%

Lead	- Maximum 0.5 ppm (0.00005%)
Silver	- Maximum 0.1 ppm (0.00001%)
Copper	- Maximum 0.1 ppm (0.00001%)
Cadmium	- Maximum 0.2 ppm (0.00002%)
Nickel	- Maximum 0.1 ppm (0.00001%)

No other impurities detected spectrographically.

The same cleaning method was used for the glass-encapsulated thermocouple since it also came into contact with the molten bismuth.

The crucible containing the charge was placed in the melting furnace and the chamber was evacuated to a pressure of about 10^{-5} Torr. The charge was then melted under this low pressure and stirred with the thermocouple tube to bring any entrapped oxide or air to the surface. The melt was then allowed to solidify and cool to room temperature. After cooling, the solid mass of bismuth was removed from the furnace and from the Pyrex crucible. A severe etching operation was performed to remove all surface impurities such as the oxide film. A solution of 75% concentrated nitric acid and 25% distilled water was used as the etchant. After etching, the bismuth was washed and dried with a clean, lint-free cloth.

The Pyrex crucible and the tip of the thermocouple tube underwent a similar acid treatment to remove all traces of bismuth and oxide impurities.

The cleaned charge and crucible were placed in the melting furnace and the bismuth was melted under a pressure of at least 10^{-5} Torr. A series of melting and freezing cycles were recorded until a consistant level

of supercooling was maintained. If the degree of supercooling was small the melt still contained some oxide impurities which had to be removed by repeating the above process. If the degree of supercooling was sufficiently large, such as about 30°C, the melt is ready for the nucleation experiment.

(D) <u>The Preparation of The Catalyst Material</u>

This section can be divided into two categories, viz.: metallic and non-metallic catalysts. Each of these types of catalysts were prepared in a different manner.

(1) <u>The Metallic Catalysts</u>

The metallic materials used as potential catalysts for this investigation are listed in Table II. The minimum purity of these materials was 99.5% and most were in the form of polycrystalline wires ranging from 0.010" to 0.031" in diameter.

The metallic wires were cut in one inch lengths and etched in a suitable acid solution to remove surface oxidation. After etching and washing, the wire was placed in a container of pure ethyl alcohol to protect it from further oxidation until it was ready to mount on the catalyst support rod. Mounting was done by means of a suitable

TABLE 2

METALLIC MATERIALS

MATERIAL	PURITY	FORM	SOURCE
Aluminum	99.5 %	Wire	A.D. MacKay, Inc.
Antimony	99.9999%	Small Chips	Electronic Space Products, Inc.
Cadmium	99.9 %	Wire	A.D. MacKay, Inc.
Cobalt	99.5 %	Wire	A.D. MacKay, Inc.
Copper	99.9 %	Wire	A.D. MacKay, Inc.
Europium	99.9 %	Chip	Ames Laboratory
Germanium	99.999 %	Chip	Electronic Space Products, Inc.
Gold	99.95 %	Wire	A.D. MacKay, Inc.
Indium	99.99 %	Chips	Indium Corporation of America
Iron	99.9 %	Wire	A.D. MacKay, Inc.
Lead	99.9999+%	Chips	Leytess Metal Corp.
Magnesium	99.9 %	Wire	A.D. MacKay, Inc.
Molybdenum	99.95 %	Wire	Fansteel
Nickel	99.5 %	Wire	A.D. MacKay, Inc.
Niobium	99.82 %	Wire	Kawecki Chem. Co.
Palladium	99.9 %	Wire	A.D. MacKay, Inc.
Platinum	99.9 %	Wire	A.D. MacKay, Inc.

Selenium	99.99 %	Chips	American Smelting and Refining Co.
Silicon	99.999 %	Needle	Electronic Space Products, Inc.
Silver	99.9 %	Wire	A.D. MacKay, Inc.
Tantalium	99.9 %	Wire	Kawecki Chem. Co.
Tellurium	99.9993%	Chips	Electronic Space Products, Inc.
Tin	99.9999%	Chips	Electronic Space Products, Inc.
Titanium	99.5 %	Wire	A.D. MacKay, Inc.
Tungsten	99.9 %	Wire	A.D. MacKay, Inc.
Vanadium	99.8 %	Wire	A.D. MacKay, Inc.
Zinc	99.9 %	Wire	A.D. MacKay, Inc.
Zirconium	99.9 %	Wire	A.D. MacKay, Inc.

glue using a 6 prong catalyst support rod as shown in Figure 9. At least 3/4 of an inch of the wire extended beyond the end of the prong of the support rod.

Those materials not in wire form were handled in a different manner. The germanium and silicon crystals were small in size and had to be mounted on the end of a glass fiber which was then mounted to the catalyst support rod.

Small chips of the indium, tin, selenium, lead, antimony and tellurium were weighed out in milligram quantities using a Thompson assay balance. These small samples were placed on the catalyst support platform of the melting furnace. Usually at least 5 chips of a single material were placed on the platform. Since all these metals easily alloy with bismuth the amount added to the melt was accurately known and could be controlled better than using a larger sample and submerging it in the melt.

(2) <u>The Non-Metallic Catalysts</u>

Table III lists the non-metallic materials used for potential catalysts in the investigation. All of these materials were in the form of powder and were mounted on a 1" long Pyrex glass fiber (about 0.02" diameter). The glass fibers were coated with an aqueous colloidal silica

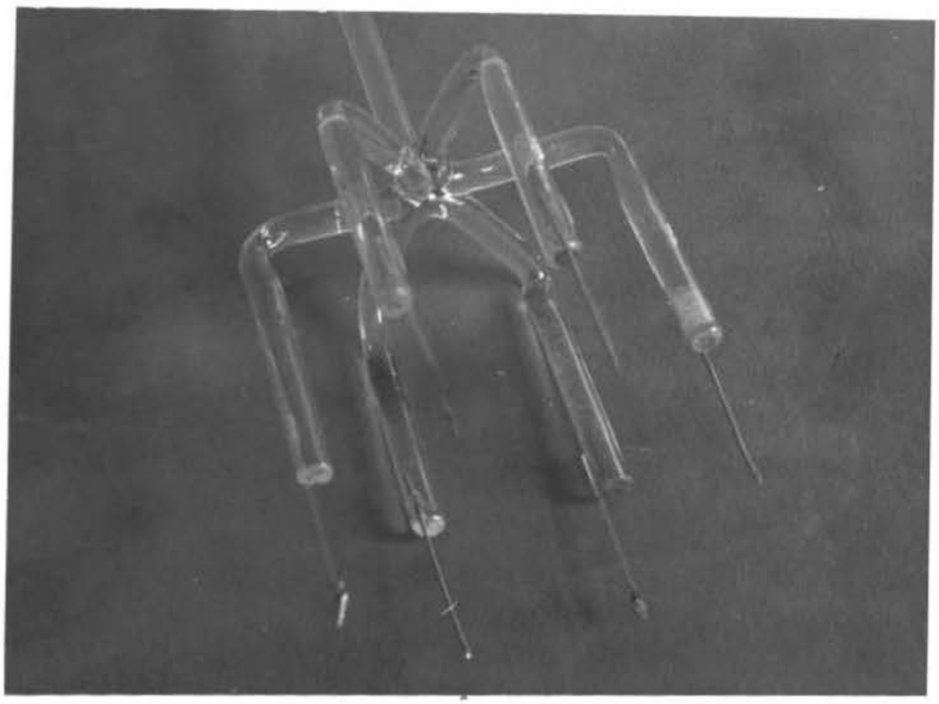


Figure 9

The 6-Prong Catalyst Support Rod

Showing The Placement of The Metalic and Non-Metallic

Materials

TABLE 3

NON-METALLIC MATERIALS

MATERIAL	FORM	SOURCE
Aluminum Oxide	powder	Aluminum Company of America
Bismuth Oxide	powder	Fisher Scientific Co.
Boron Carbide	powder	A.D. MacKay, Inc.
Graphite	powder	Fisher Scientific Co.
Silicon dioxide	powder	Ottawa Silica Company
Titanium Carbide	powder	A.D. MacKay, Inc.
Zirconium Boride	powder	Borolite Corp.
Zirconium Carbide	powder	A.D. MacKay, Inc.
Zirconium Hydride	powder	Metal Hydrides, Inc.
Zirconium Nitride	powder	Metal Hydrides, Inc.
Zirconium Oxide	powder	Fisher Scientific Co.
Zirconium Silicate	powder	Continental Mineral Processes, Inc.

solution and while wet were immersed into the dry powder. The powder completely coated the end of the fiber and was allowed to dry for a period of at least 2 hours.

The fibers were then mounted on the catalyst support rod in the same manner as the metallic catalysts.

(E) The Melting and Solidification Procedure

(1) Vacuum Deoxidation of the Melt

It was found that the supercooling of a bismuth melt could be increased if the melt was deoxidized by heating to about 400-500°C under a vacuum of at least 10^{-5} Torr. The end point of the deoxidation procedure was noted when the bismuth coated the inside wall of the Pyrex furnace housing. The temperature of the melt at these higher temperatures could not be measured due to the limitation in the type of thermocouple used, thus rough extrapolations were made from the strip-chart paper when the pen went off scale. This deoxidation technique was necessary in order to increase the amount of background supercooling of a new melt. Without vacuum deoxidization at these higher temperatures (melting point of bismuth is 271.3°C) some oxide remained on the surface of the melt. The removal of this oxide film reveals a mirror-like surface on the melt.

(2) The Introduction of the Controlled Atmosphere

The procedure used when an atmosphere was necessary, was to evacuate the system to below 10^{-3} Torr and then flush the furnace with the desired atmosphere, through the inlet on the furnace cover, until a positive pressure was obtained. A bubble tube was used to indicate a flow of gas through the furnace. This bubble tube was located at the exhaust end of the system and the gas passing through the bubble tube was expelled through a rubber tube extending out into the open atmosphere (outside the building). Dibutyl phthalate was used as the bubble tube liquid due to its low vapor pressure.

Before the melting operation, the system is flushed for a minimum of 2 hours with the controlled atmosphere to insure removal of most of the oxygen.

(3) The Introduction of The Catalysts Into The Melt

The high-purity bismuth was melted under either vacuum or a controlled atmosphere and allowed to freeze while the temperature cycle was plotted on the strip chart recorder. When a fairly consistent supercooling was obtained (after about 3 or 4 cycles) the melt was ready to receive the foreign material. When the melt reached a

superheat of 20°C on the cooling cycle, the catalyst was inserted into the melt to a depth of 4 mm. This depth was selected since it is the same depth as the thermocouple. A millimeter scale was attached to the portion of the thermocouple and the catalyst support rod extending outside the furnace cover so that fairly accurate depth measurements could be maintained. The 20°C superheat was ample to bring the temperature of the catalyst near to the temperature of the melt, thus preventing a chilling effect around the catalyst which in turn could promote premature nucleation and a small supercooling value.

A number of melting and freezing cycles were recorded with and without the catalyst in contact with the melt. Enough cycles with the catalyst immersed in the melt were made so that the effect, if any, of the catalyst on the supercooling behavior of the bismuth was measured. Usually a minimum of 4 cycles with the catalyst immersed in the melt were recorded.

The same melt was used for more than one catalyst if no effect on the supercooling behavior of the melt was detected. This procedure saved time since more than one catalyst could be included in the melting furnace without interupting the vacuum or controlled atmosphere.

When the catalyst was used on the catalyst support platform, instead of the catalyst support rod, a different technique was employed. In this case, after obtaining a constant background supercooling value, the catalyst was pushed off the platform into the superheated melt by means of a copper wire mounted on the end of the catalyst support rod. The catalyst was then stirred into the molten bismuth with the thermocouple tube. This technique was used for those metallic catalysts that alloyed easily with bismuth (In, Pb, Se, Cd, Te, Sb, etc.). Several additions of each metal were made in the same experiment. During each cycle the melt was stirred to distribute the catalyst throughout the melt. A new melt was used for each experiment involving this type of a catalyst.

IV. EXPERIMENTAL RESULTS

In general, this investigation concerns itself with a study of the effect of varying conditions on the supercooling behavior of high-purity liquid bismuth. These varying conditions include the melting atmosphere, the superheat above the melting temperature of bismuth and the intentional addition of both metallic and non-metallic substances to the bismuth melt. The results will therefore be categorized according to the following:

(A) The effect of various atmospheres on the supercooling behavior of liquid bismuth.

(B) The effect of varying the degree of superheat on the supercooling behavior of liquid bismuth.

(C) The effect of various non-metallic foreign substances on the supercooling behavior of liquid bismuth.

(D) The effect of various metallic foreign substances on the supercooling behavior of liquid bismuth.

(A) The Effect of Various Atmospheres on The Supercooling Behavior of Liquid Bismuth

In this investigation three different gaseous atmospheres and vacuum were employed to establish the effect, if any,

the furnace surroundings have on the supercooling behavior of bismuth. The atmospheres used were air, argon and hydrogen and the results of each type of atmospheric condition will be discussed individually.

(1) Melting Under a Vacuum

In this study a fairly constant pressure of between 10^{-5} to 10^{-6} Torr could be maintained during an experimental run which consisted of several melting and freezing cycles. Before melting in a vacuum much of the bismuth oxide surface film was removed by a suitable etching process. After this oxide removal technique was employed, a degree of supercooling of the melt on the order of about 17 to 22°C was obtainable. The normal vacuum-melting process was not sufficient in removing all of the oxide film on the melt surface. Possibly at these pressures enough oxygen is present in the system to cause surface oxidation or the surface oxidation was not sufficiently removed during the etching treatment. The latter condition seems quite plausible from the following results.

By melting under a vacuum at a superheat on the order of 200 to 300°C the surface oxide film was essentially dissipated. This process is a vacuum deoxidation process which allows the oxide film to dissociate or evaporate under

this low pressure and relatively high temperature. During the vacuum deoxidation process the bismuth was allowed to evaporate and condense on the colder portions of the furnace housing. In this vapor deposition process the oxide film is carried along with the bismuth vapor to these colder regions of the furnace. Some thermodynamic dissociation can also take place at these temperatures.

After vacuum deoxidation the bismuth melt could be supercooled to a maximum of about 35°C. This indicated that by partially removing this oxide layer a greater degree of supercooling is obtainable in the bismuth melt. Complete removal of the oxide film was never obtained after vacuum deoxidation.

(2) <u>Melting Under an Argon Atmosphere</u>

The results of melting and freezing under an argon atmosphere were similar to those obtained by the vacuum-melting process. Argon being an inert atmosphere did not noticeably alter the oxide film on the surface of the melt. By first vacuum-melting and then melting the same charge under argon, the range of supercooling was not noticeably changed.

The advantage in using a gaseous atmosphere to a vacuum is the total elimination of vibrations that are caused by

the mechanical pumping system. By comparing the results of the supercooling of bismuth under vacuum and under an argon atmosphere the slight mechanical vibrations that were created by the vacuum system had no effect on the supercooling behavior.

A noticeable effect of melting under a gaseous atmosphere as opposed to vacuum melting is the change in cooling rate of the melt. For example, under a vacuum (10^{-6} Torr) the cooling rate of a 60 gram melt of bismuth was about 12°C/min., while under argon the cooling rate increased to about 27°C/min. This cooling rate could also be altered by changing the design and materials used for the resistance furnace. It was found that this change in cooling rate did not alter the supercooling behavior of the melt.

(3) <u>Melting Under a Hydrogen Atmosphere</u>

A hydrogen atmosphere was used during the melting process to chemically reduce the oxide surface film on the melt. The results of the hydrogen reduction process were quite successful.

After vacuum deoxidation to obtain a background supercooling of between 25 to 35°C the hydrogen reduction was effective in increasing the supercooling to a maximum value

of about 46°C. The hydrogen atmosphere was allowed to pass over the liquid bismuth at a superheat of about 100°C for a period of at least an hour.

Once the surface of the melt appeared bright, with a mirror-like finish, indicating the removal of the oxide film, this high degree of supercooling can be obtained. The melt during the solidification process freezes rather quickly whereas without the proper removal of the oxide film the freezing process was much slower. Usually dendritic growth was observed on the surface of the melt containing an oxide layer thus indicating that nucleation had taken place at the surface or near the surface. When the surface film was removed by proper hydrogen reduction, dendritic growth on the surface was not observed.

Due to the success of the use of a hydrogen atmosphere in removing the oxide surface film on the bismuth melt this atmosphere was employed for the bulk of the nucleation experiments involving the addition of foreign materials to the melt.

The cooling rate for a 60 gram bismuth melt in a hydrogen atmosphere was about 40°C/min.

(4) Melting Under an Air Atmosphere

An experimental run was performed in which approximately 60 grams of high purity bismuth was melted in the open atmosphere. The results of this run can be seen in table 4 for several freezing and melting cycles. As can be seen, the average supercooling obtainable was 6.0°C under these conditions. A marked change can be seen in the supercooling below a superheat of about 15°C.

During the melting process a thick surface oxide layer formed on the melt. As soon as this surface layer is removed, a fresh new layer instantly forms indicating that bismuth melted in the open atmosphere is always in contact with an oxide-layer. Previous investigators[25, 33, 34] have also found that the air melting process imposes a limit on the amount of supercooling obtainable for a given bismuth melt.

It was found that during air melting a cooling rate of about 27°C/min. is obtainable.

To summarize the results of the effect of various atmospheres on the supercooling behavior of bismuth a schematic diagram as shown in figure 10 has been constructed. This diagram shows the supercooling limitation imposed on the bismuth melt under the various melting conditions

TABLE 4

DATA FOR MELTING BISMUTH IN AN AIR ATMOSPHERE

Freezing Cycle No.	Superheat °C	Supercooling °C
1	72.4	6.4
2	70.4	6.7
3	61.8	6.4
4	56.0	5.4
5	45.8	5.4
6	39.4	5.4
7	37.1	7.0
8	35.5	6.4
9	35.2	5.1
10	27.5	5.4
11	15.0	5.4
12	12.8	4.2
13	11.2	3.5
14	9.6	3.2
15	6.0	1.6

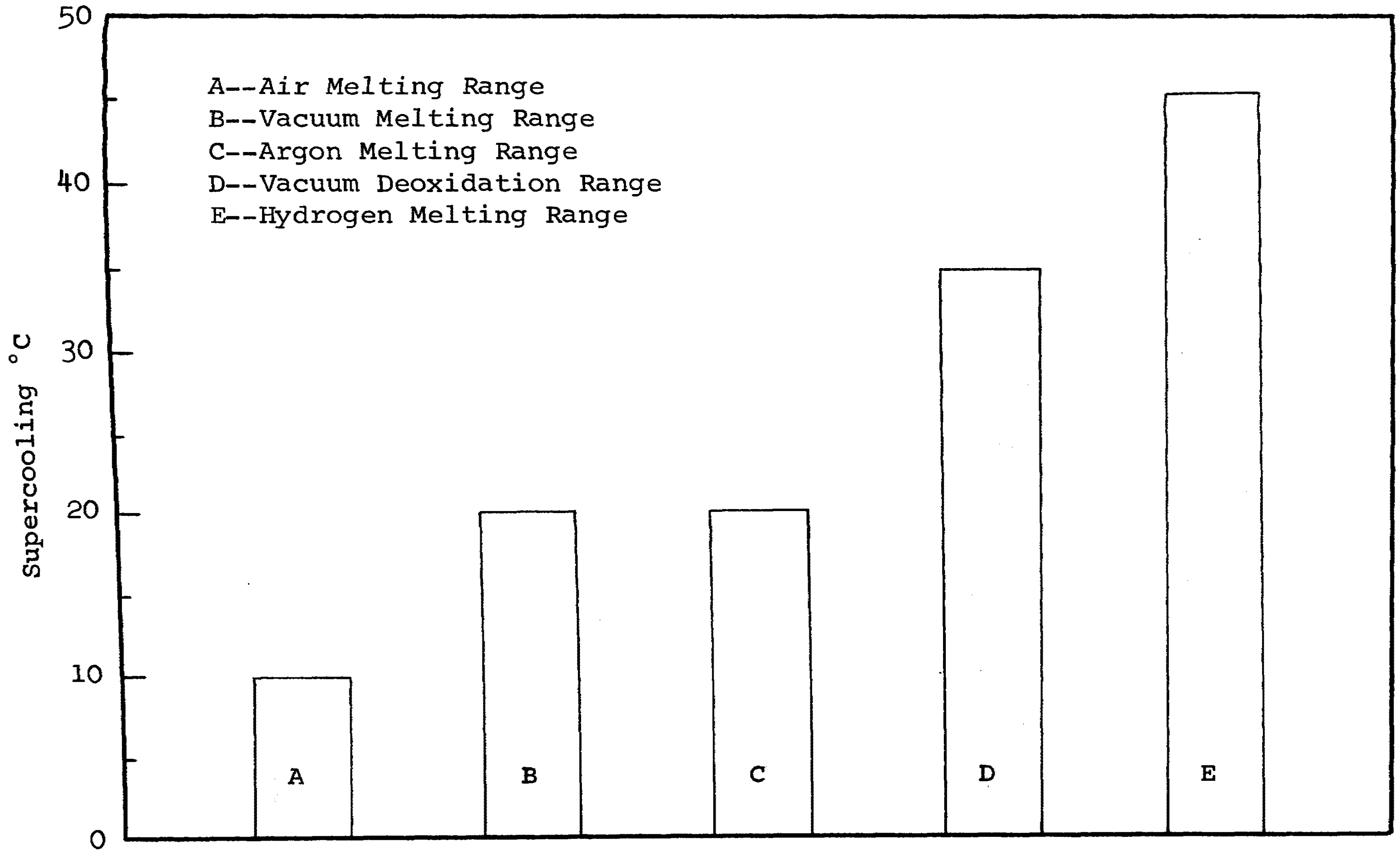


Figure 10. The Effect of Melting Conditions on the Supercooling Behavior of High-Purity Liquid Bismuth

studied in this investigation. In order to increase the supercooling above that obtainable under a hydrogen atmosphere a flux must be used on the surface of the melt. By using a stannous chloride flux[34] the supercooling value approaches 90°C in some cases, and in very small melts about 120°C supercooling have been obtained using a ternary tin, thallium and zinc chloride flux[33]. This type of technique was not used in this investigation.

(B) <u>The Effect of Varying The Degree of Superheat on The Supercooling Behavior of Liquid Bismuth</u>

The amount of superheat was found to be of concern only for melts of bismuth that were melted in air where it was found that superheats of less than about 15°C decreased the degree of supercooling obtainable. Above 15°C superheat, the background supercooling value maintained a somewhat constant value. This data can be found in table 4. A plot of superheat vs. supercooling for an air melt of bismuth is shown in figure 11. Since this phenomenon was observed by previous investigators[24, 33, 34] it was not studied in detail in the present investigation.

The amount of superheat for melts of bismuth under vacuum, argon and hydrogen was not a critical factor and no observable changes in supercooling were found with varying degrees of superheat.

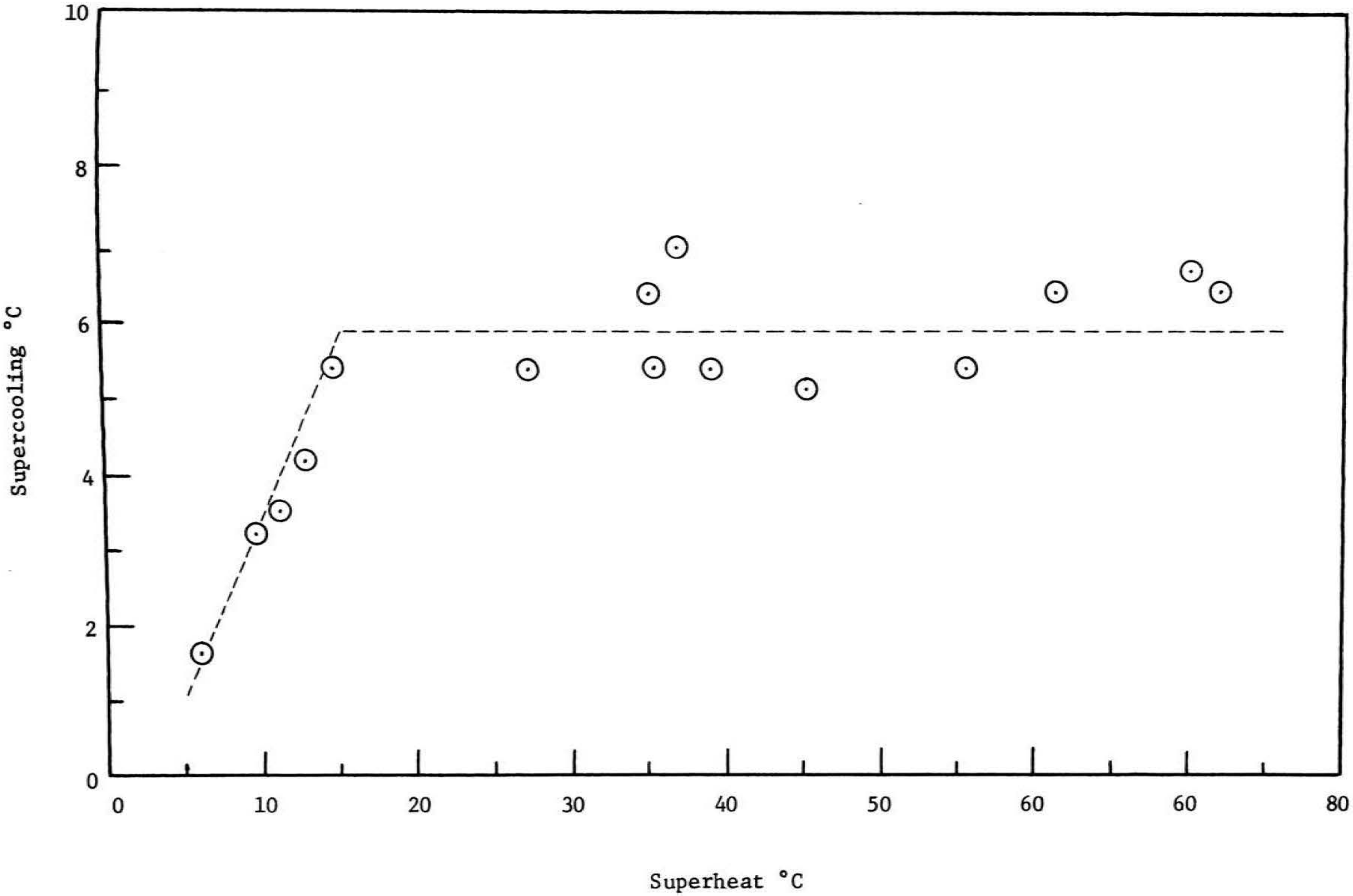


Figure 11. The Effect of Superheat on The Supercooling Behavior of Liquid Bismuth

(c) The Effect of Various Non-Metallic Foreign Substances On The Supercooling Behavior of Liquid Bismuth

It was found that the 12 non-metallic substances listed in table 3 had no effect on the supercooling behavior of bismuth when intentionally added to the melt. The data and graphical results of the supercooling behavior of a typical non-metallic foreign material, boron carbide, can be found in table 5 (Appendix) and Figure 12. The plot of supercooling vs. freezing cycle is just a graphical representation of the supercooling data taken from the strip-chart recording. The dotted line in each graph indicates the average background supercooling. The background supercooling in this case is the supercooling value measured in the absence of the intentionally added foreign substances in the melt.

An interesting feature of this phase of the investigation is to note that bismuth oxide, Bi_2O_3, did not cause nucleation of the bismuth melt. This tends to indicate that only a natural occurring surface film acts as a more effective catalytic agent in promoting nucleation than a chemically formed bismuth oxide intentionally added to the melt.

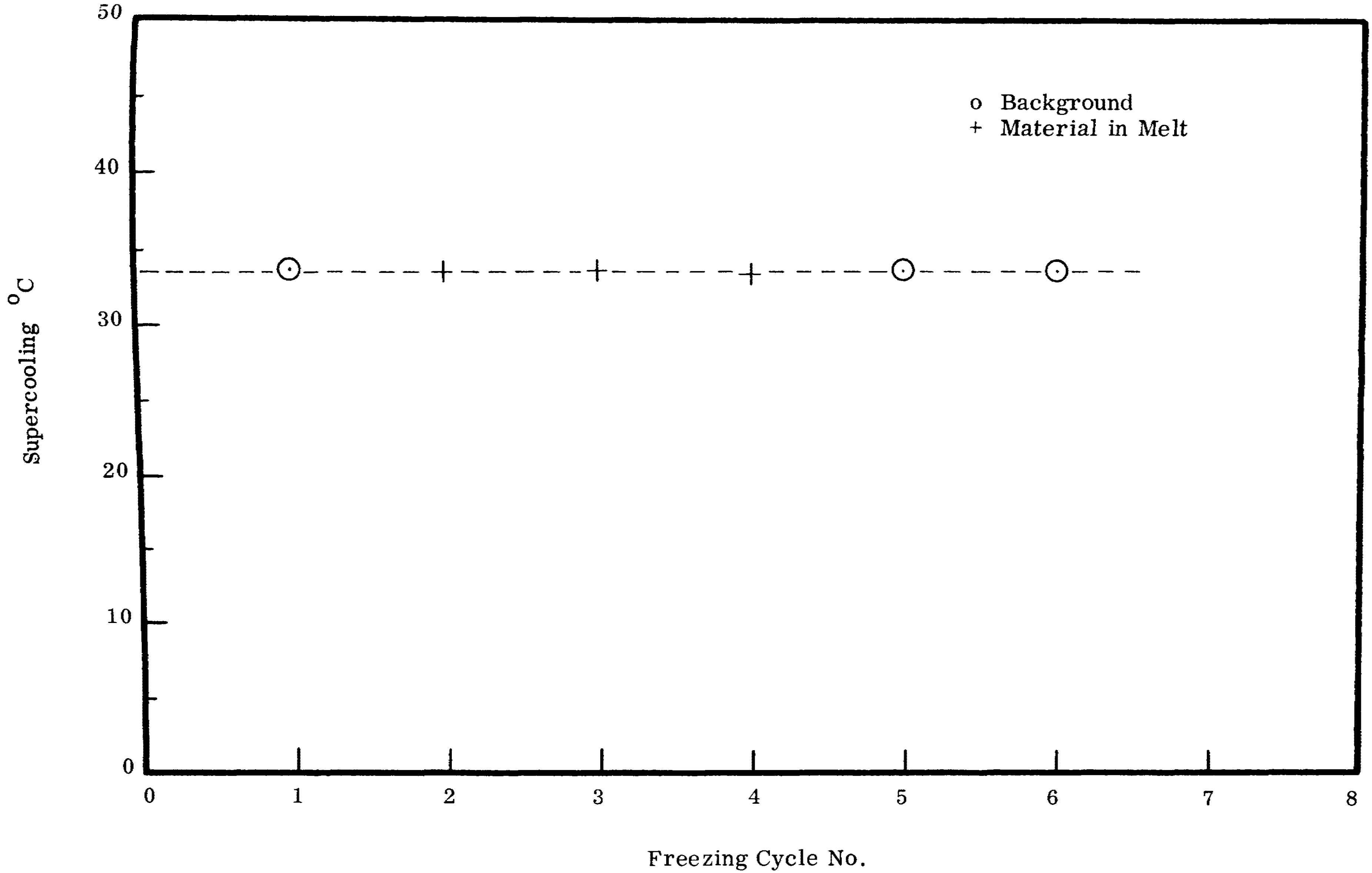


Figure 12. The Effect of Boron Carbide on The Supercooling Behavior of Bismuth

(D) <u>The Effect of Various Metallic Foreign Substances On The Supercooling Behavior of Liquid Bismuth</u>

The metallic substances intentionally added to a bismuth melt are listed in table 2 along with their purity and form. It was found that only a few of the 28 metallic elements added to a bismuth melt altered the supercooling behavior. Therefore, the results will be divided into two groups, namely: (a) metals that did not alter the supercooling behavior of bismuth, and (b) metals that did alter the supercooling behavior.

(1) <u>Metals That Did Not Alter The Supercooling Behavior of Liquid Bismuth</u>

Of the 28 metals studied, as possible catalytic materials for a bismuth melt, 19 were found not to effect the supercooling behavior. These metals are:

Aluminum

Cobalt

Europium

Germanium

Iron

Magnesium

Molybdenum

Nickel

Niobium

Palladium

Platinum

Silicon

Tantalum

Tin

Titanium

Tungsten

Vanadium

Zinc

Zirconium

The tabulated and graphical results for a typical material, tin, can be seen in table 6 (Appendix) and figure 13.

Of these 19 elements only 2 were found to alloy completely with the molten bismuth, namely, palladium and tin. The other 17 elements did not noticeably alloy with the bismuth melt. For the palladium experiment 153 ppm were dissolved in the melt and for the tin experiment a total of 152 ppm were dissolved. In the case of the tin addition a plot of tin concentration vs. supercooling is shown in figure 14. As can be seen from this data tin had no effect on the supercooling behavior of bismuth. Similar results were obtained with palladium additions.

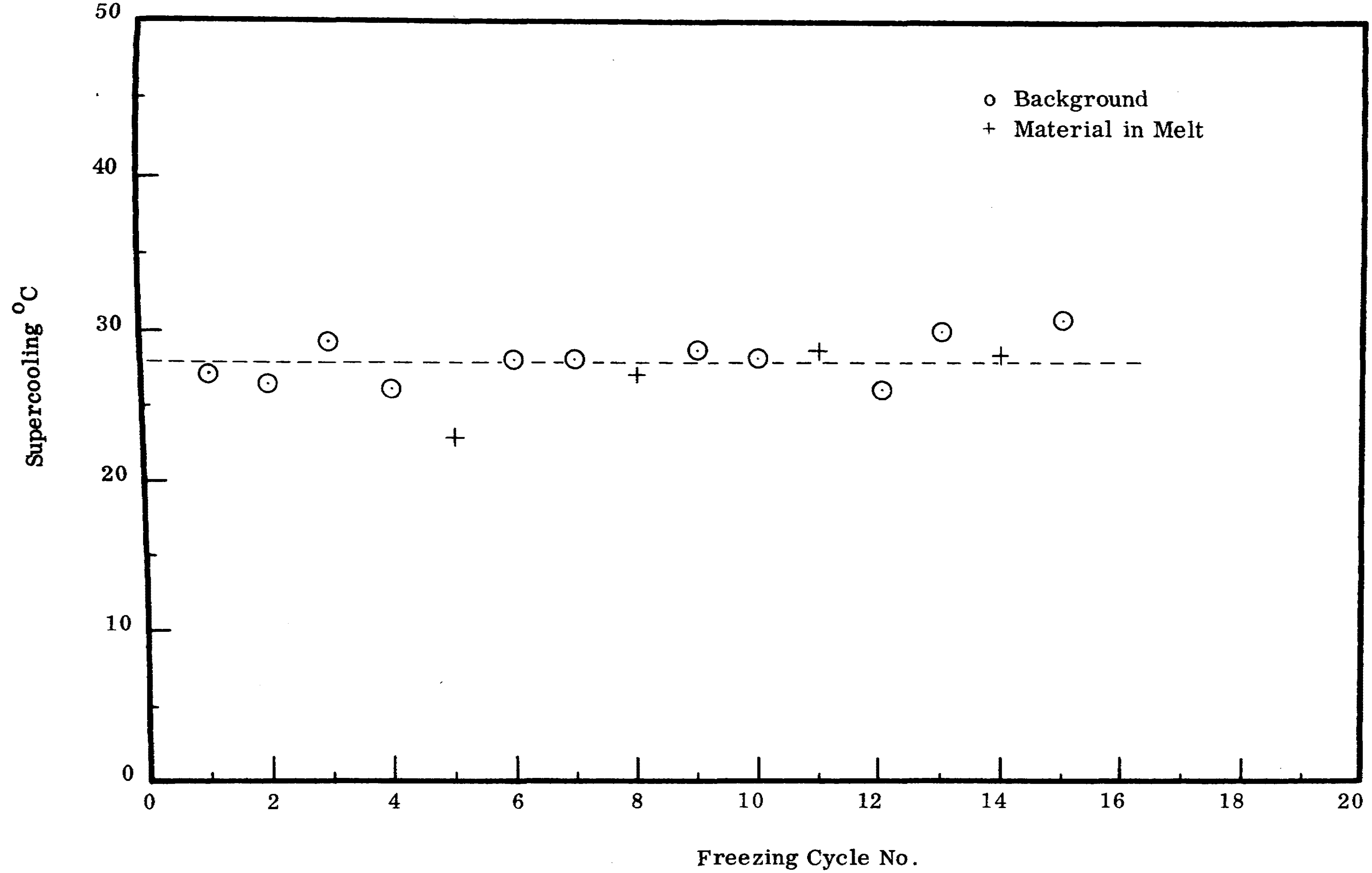


Figure 13. The Effect of Tin Additions on The Supercooling Behavior of Bismuth

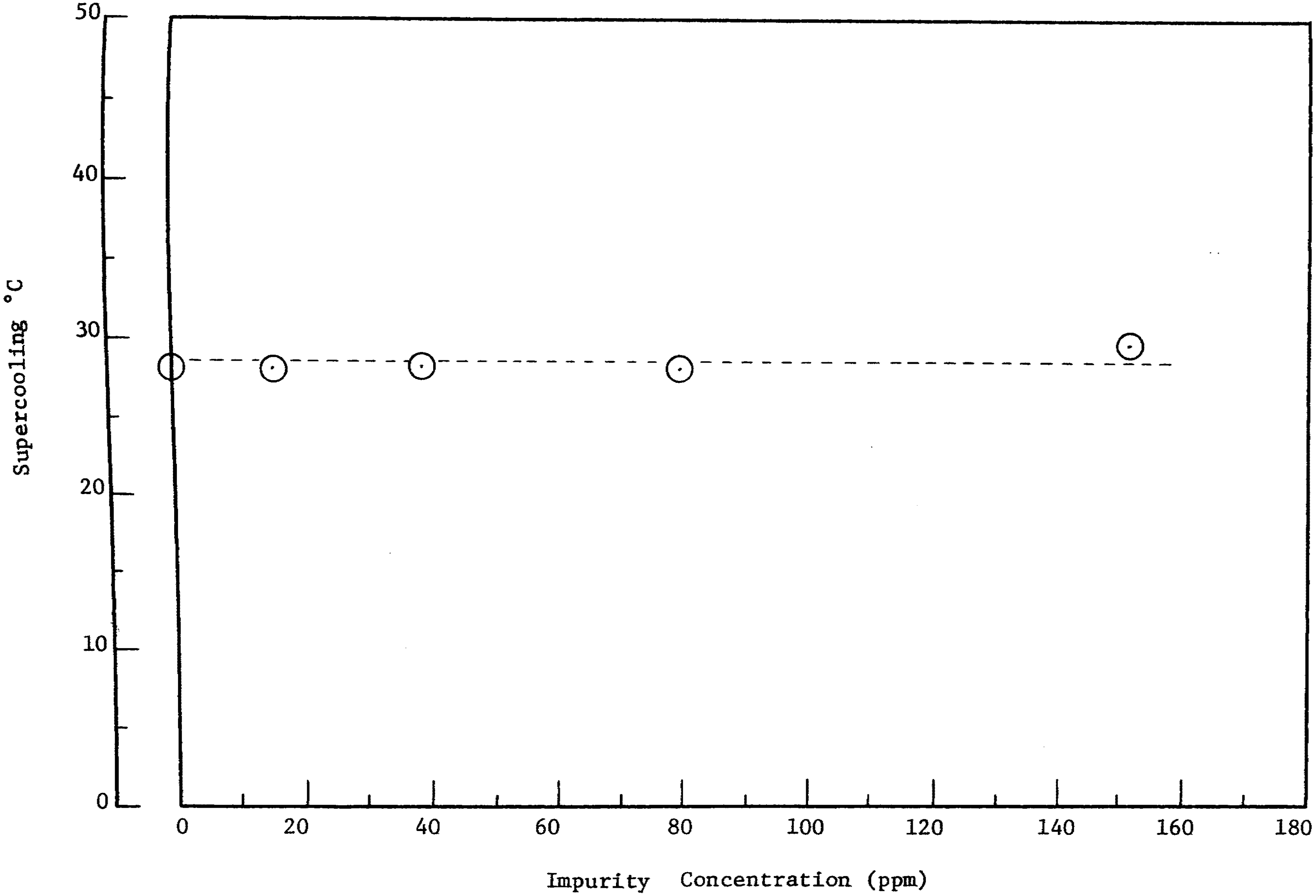


Figure 14. The Relationship Between Tin Concentration and The Supercooling Behavior of High-Purity Liquid Bismuth

(2) Metals That Altered The Supercooling Behavior Of Liquid Bismuth

Of the 28 metals employed only 9 affected the degree of supercooling of molten bismuth. These metals are:

Antimony

Cadmium

Copper

Gold

Indium

Lead

Selenium

Silver

Tellurium

The effect on the supercooling behavior of bismuth can be classified as drastic, moderate or slight. Those elements having a drastic effect on the supercooling behavior were antimony and tellurium; those classified as having a somewhat moderate effect are selenium and indium; and those having a slight effect are gold, silver, copper, lead and cadmium.

All of these elements except copper completely alloyed with the liquid bismuth. The copper wire only partially alloyed upon insertion in the melt.

The results of intentionally adding antimony to a bismuth melt are shown in table 7 (Appendix) and figure 15. The upper dotted line in the figure represents the average background supercooling, 36.5°C, of the bismuth melt before the addition of antimony. The lower line represents the average background supercooling, 4.1°C, after the 5 additions of antimony were made. The background supercooling produced by the first antimony addition (cycles 5 and 6 were not used in calculating the average background supercooling since they were not representative of the other cycles. In this investigation the average background supercooling after an intentional addition has been made is the characteristic supercooling for that material.

Figure 16 shows a plot of antimony concentration in parts per million (ppm) in the bismuth melt vs. supercooling. As can be seen, an addition of only 3.2 ppm drastically changed the supercooling of pure bismuth. With further additions of antimony the characteristic supercooling reached a somewhat constant value of 4.1°C. The values of supercooling used for this plot are the average background supercooling obtained after each addition of antimony was made.

The results of intentionally adding tellurium to the bismuth melt are shown in table 8 (Appendix) and figure 17.

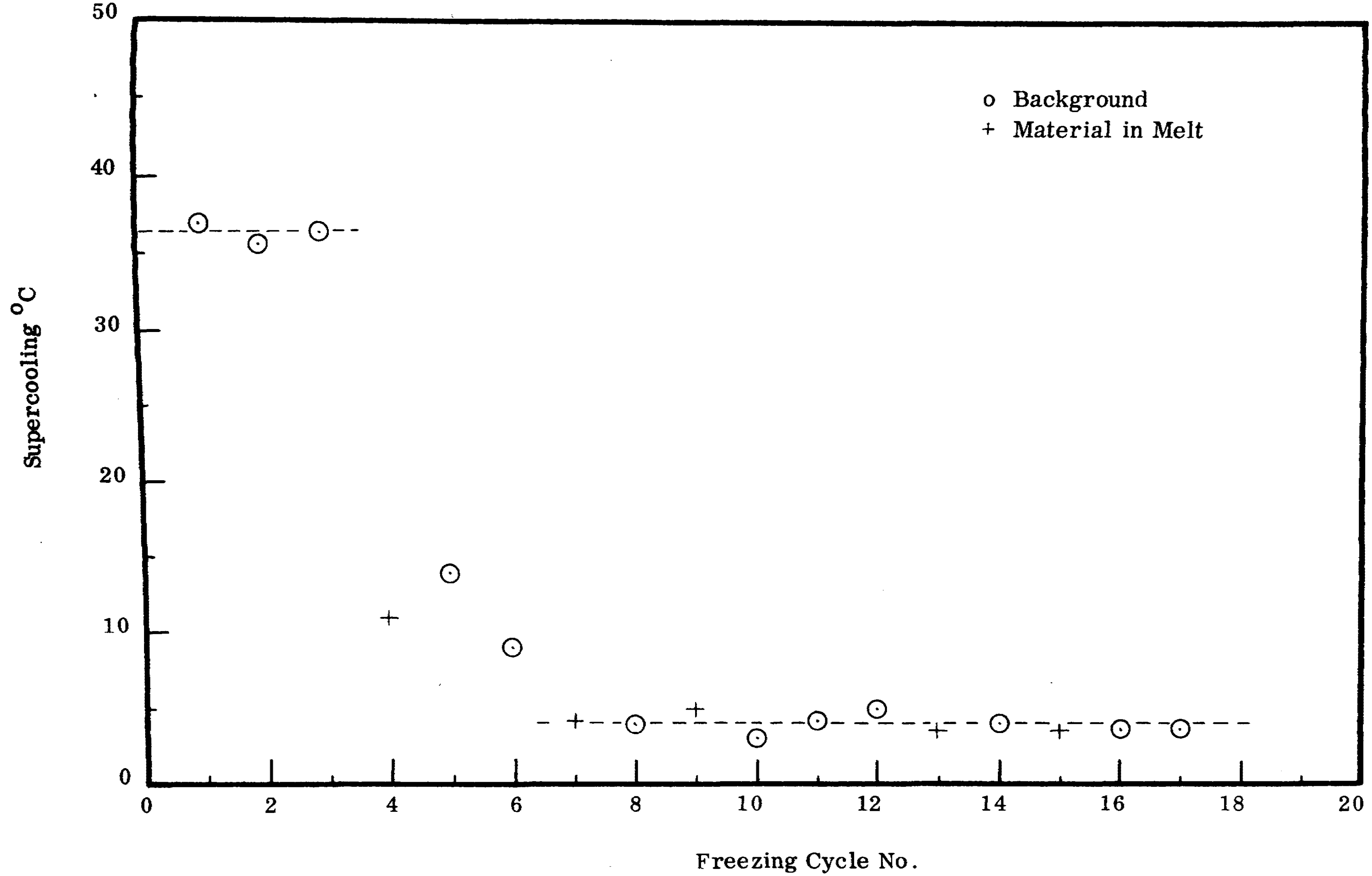


Figure 15. The Effect of Antimony Additions on The Supercooling Behavior of Bismuth

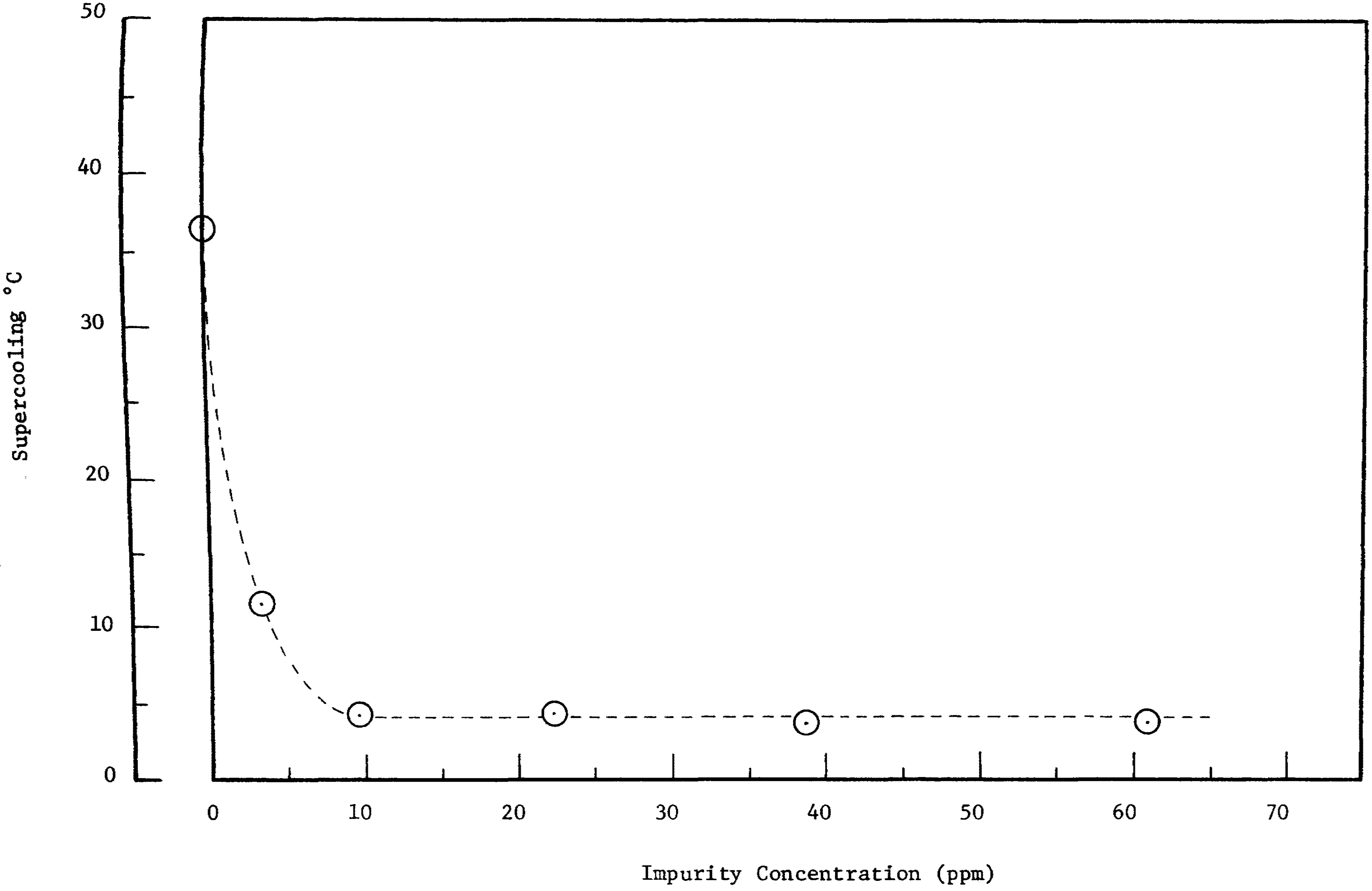


Figure 16. The Relationship Between Antimony Concentration and The Supercooling Behavior of High-Purity Liquid Bismuth

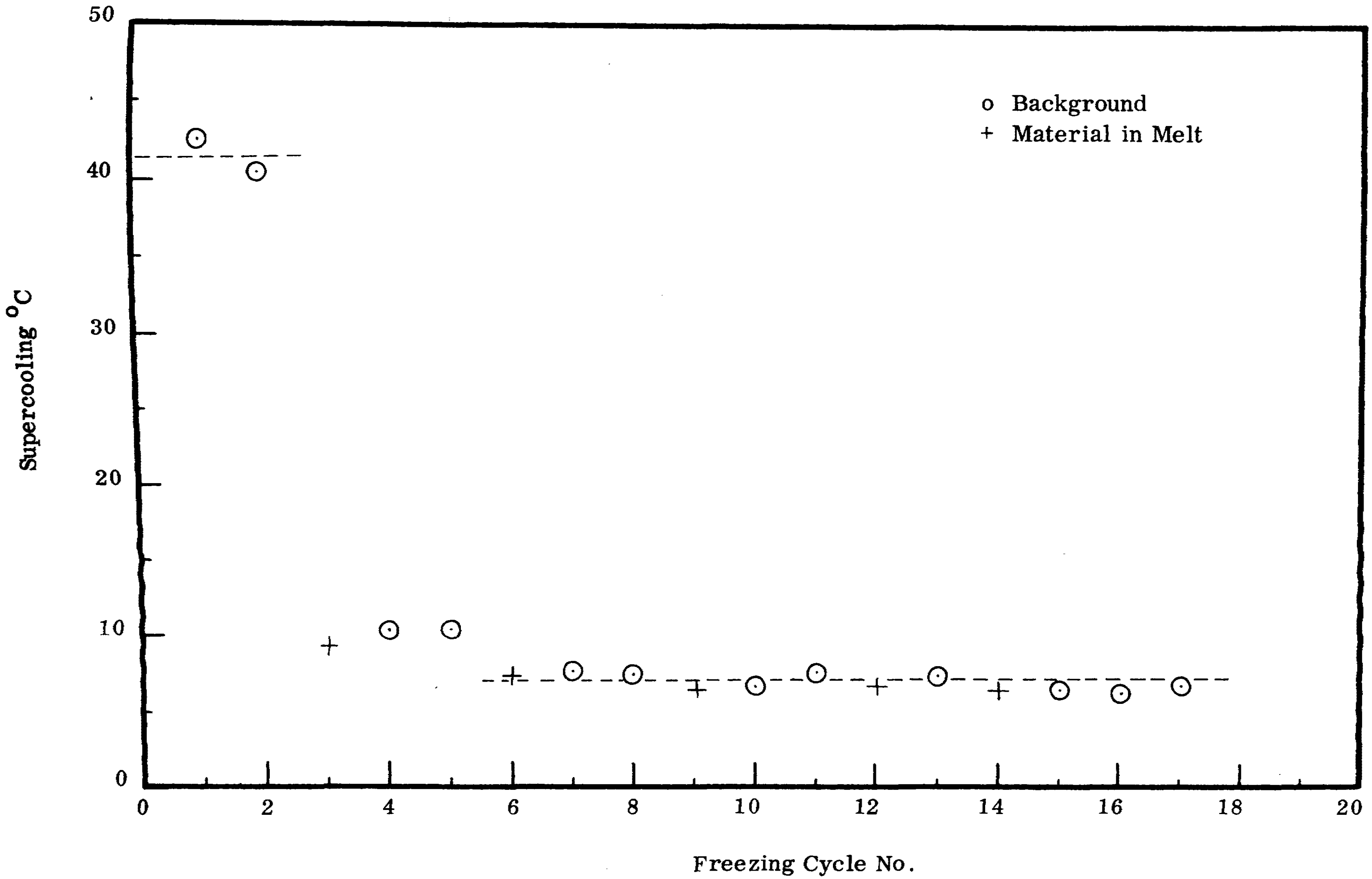


Figure 17. The Effect of Tellurium Additions on The Supercooling Behavior of Bismuth

The average background supercooling before adding the tellurium was 41.6°C. This average supercooling was changed to 7.3°C by the addition of small amounts of tellurium to the melt. As in the case of the antimony addition the first tellurium addition was not included in the average background supercooling after alloying had occurred.

Tellurium concentration (ppm) vs. supercooling is shown in figure 18. The first addition of 3.9 ppm tellurium decreased the background supercooling by about 75%.

Table 9 (Appendix) and figure 19 give the results of small additions of selenium in a bismuth melt. In the case of selenium the background supercooling of 29.0°C was obtained before intentional additions were made. It can be seen, however, that the background supercooling after selenium additions were made was decreased to an average of 14.2°C for its characteristic supercooling value.

A plot of selenium concentration vs. supercooling is shown in figure 20. As can be seen, the selenium additions had a moderate effect on changing the supercooling of bismuth as compared to the effect of both antimony and tellurium.

The results of small indium additions can be seen in table 10 (Appendix) and figure 21. The average background supercooling of 26.7°C was changed to an average of 12.3°C by intentionally adding indium to the melt. Again as in

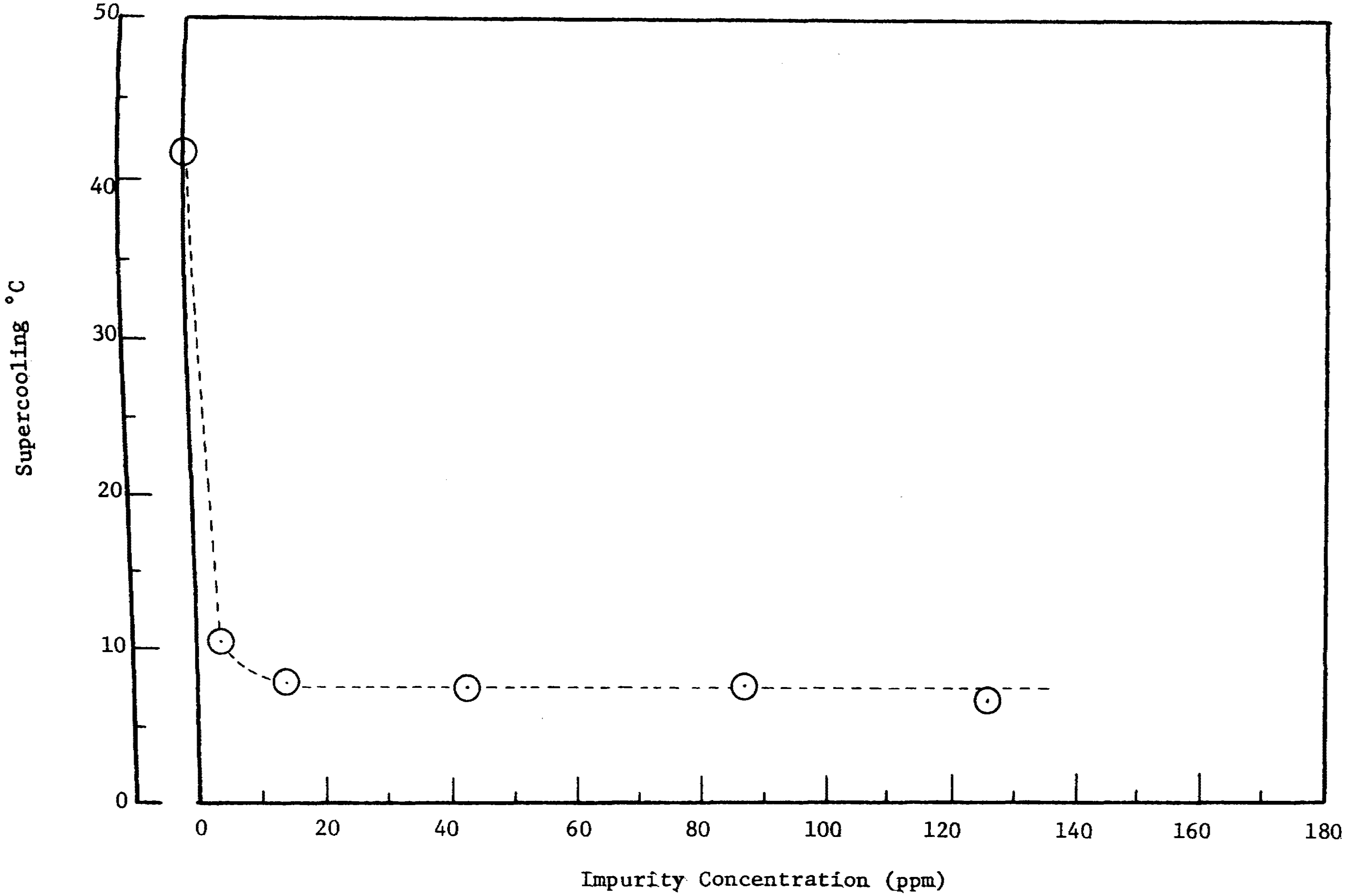


Figure 18. The Relationship Between Tellurium Concentration and The Supercooling Behavior of High-Purity Liquid Bismuth

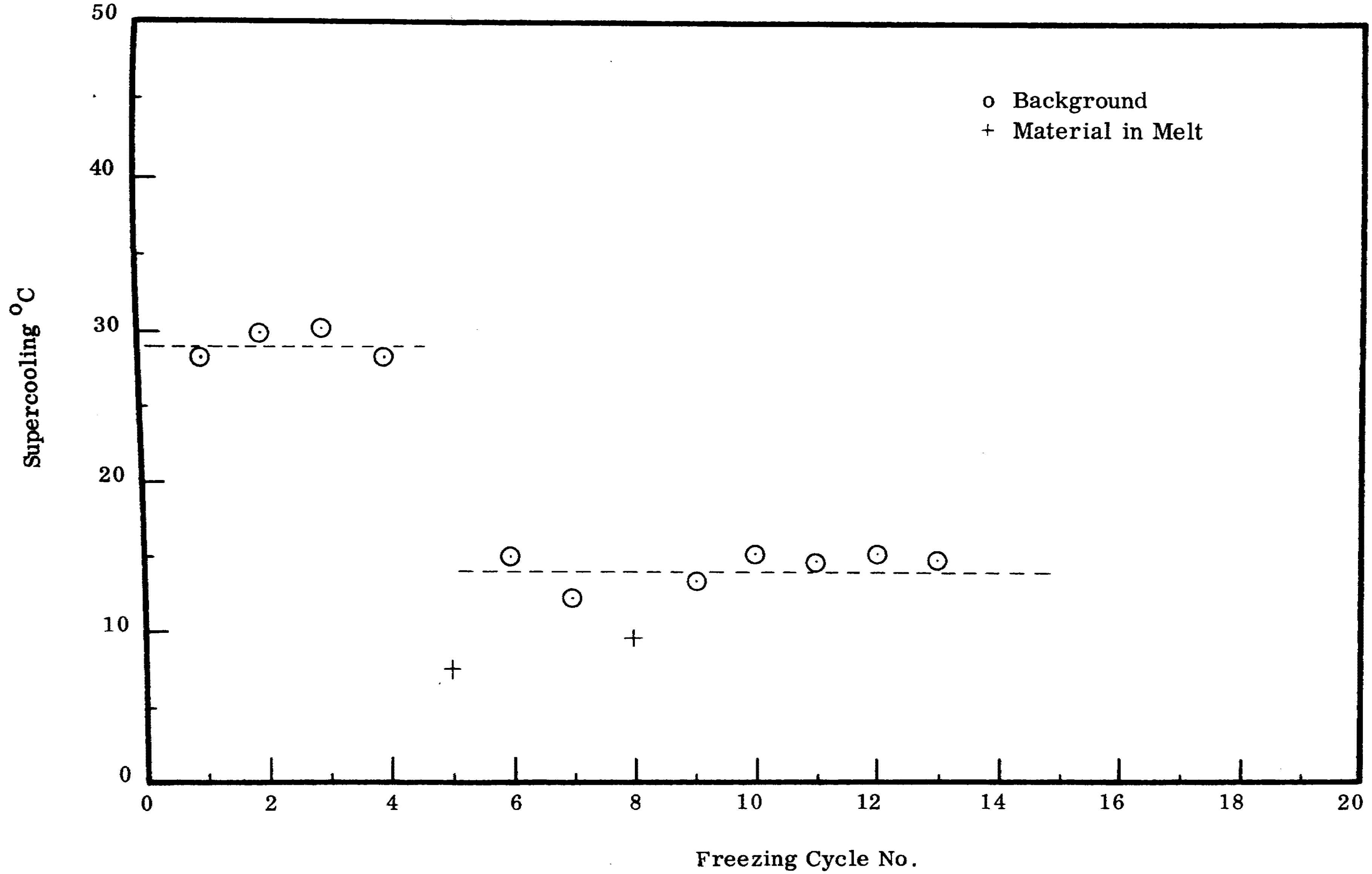


Figure 19. The Effect of Selenium Additions on The Supercooling Behavior of Bismuth

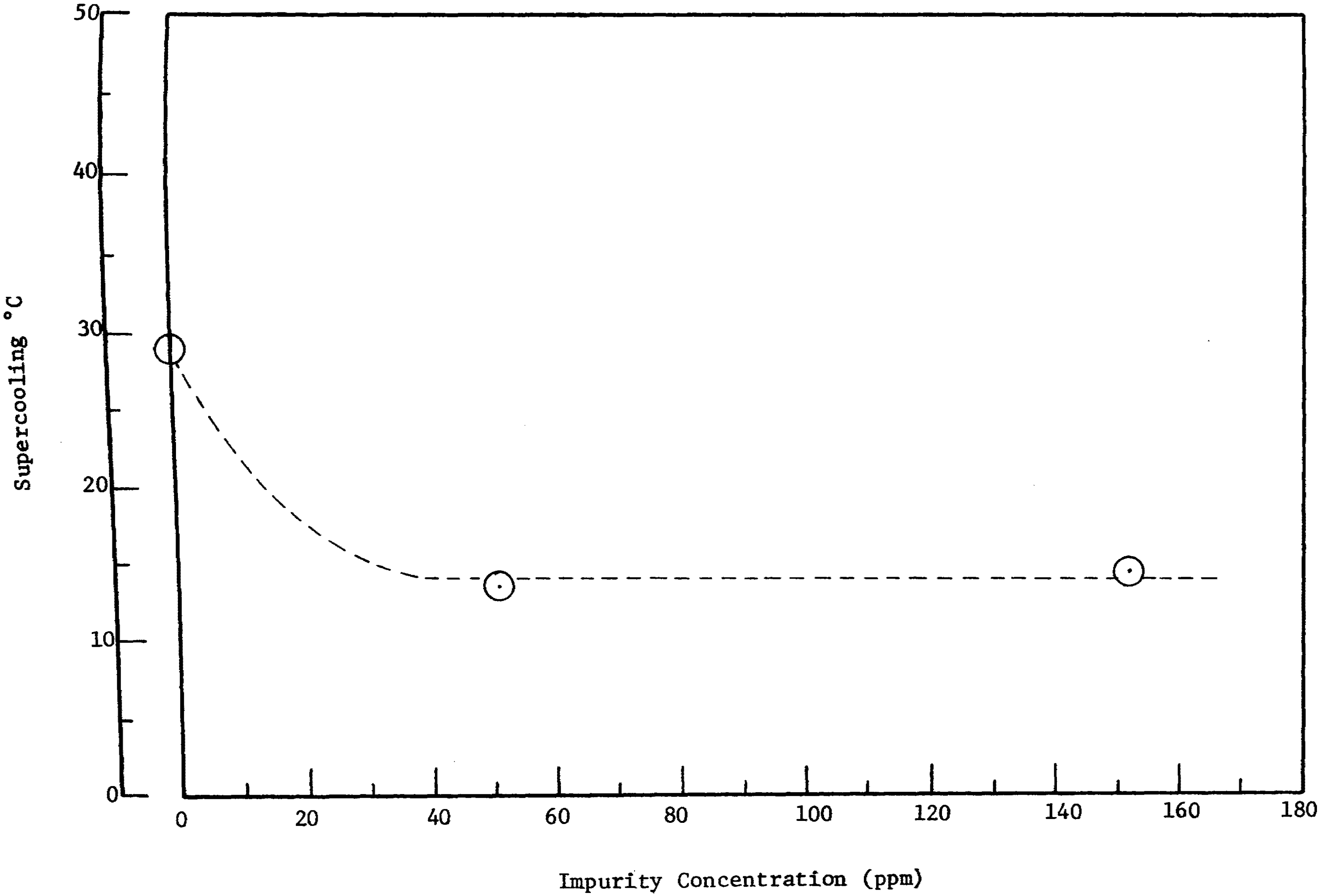


Figure 20. The Relationship Between Selenium Concentration and The Supercooling Behavior of High-Purity Liquid Bismuth

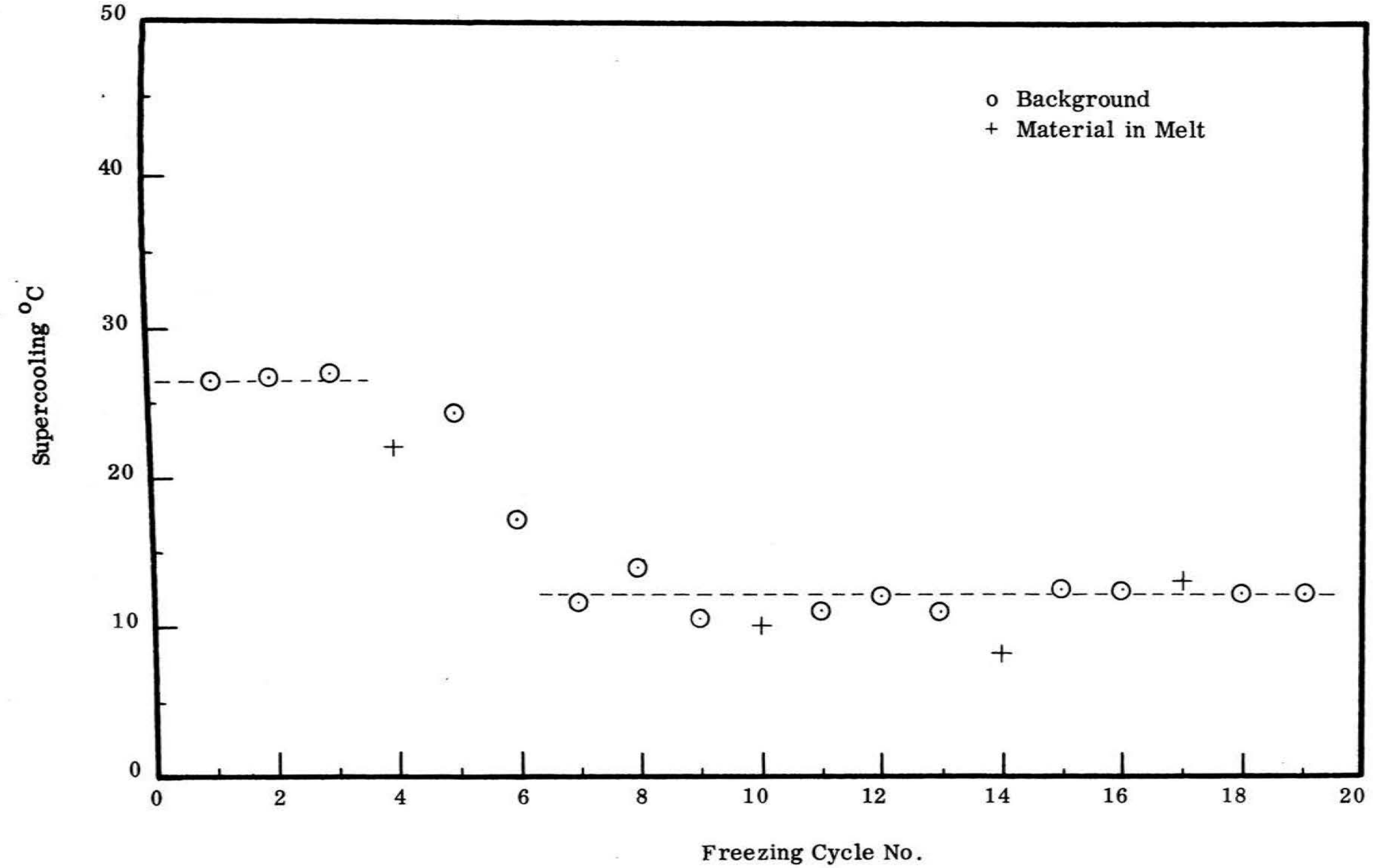


Figure 21. The Effect of Indium Additions on The Supercooling Behavior of Bismuth

the case for antimony and tellurium the effect of the first addition was not included in the average background supercooling of 12.3°C.

A plot of indium concentration vs. supercooling can be seen in figure 22. As in the case of selenium additions, the indium had a moderate effect on the supercooling behavior of bismuth.

Cadmium additions to a pure bismuth had a measureable effect on the supercooling behavior of pure bismuth since the average background supercooling of 30.4°C was changed to an average value of 20.4°C as shown in table 11 (Appendix) and figure 23. A plot of cadmium concentration vs. supercooling can be seen in figure 24.

Lead additions had a similar effect on the supercooling behavior of pure bismuth. The average background supercooling of the pure bismuth was maintained at 34.3°C. After the addition of small amounts of lead to the melt the background supercooling level was changed to 22.4°C. This can be seen in the tabulated data in table 12 (Appendix) and figure 25. A plot of the lead concentration vs. supercooling is shown in figure 26.

Additions of gold, silver and copper had a slight effect on the supercooling behavior of pure bismuth. The

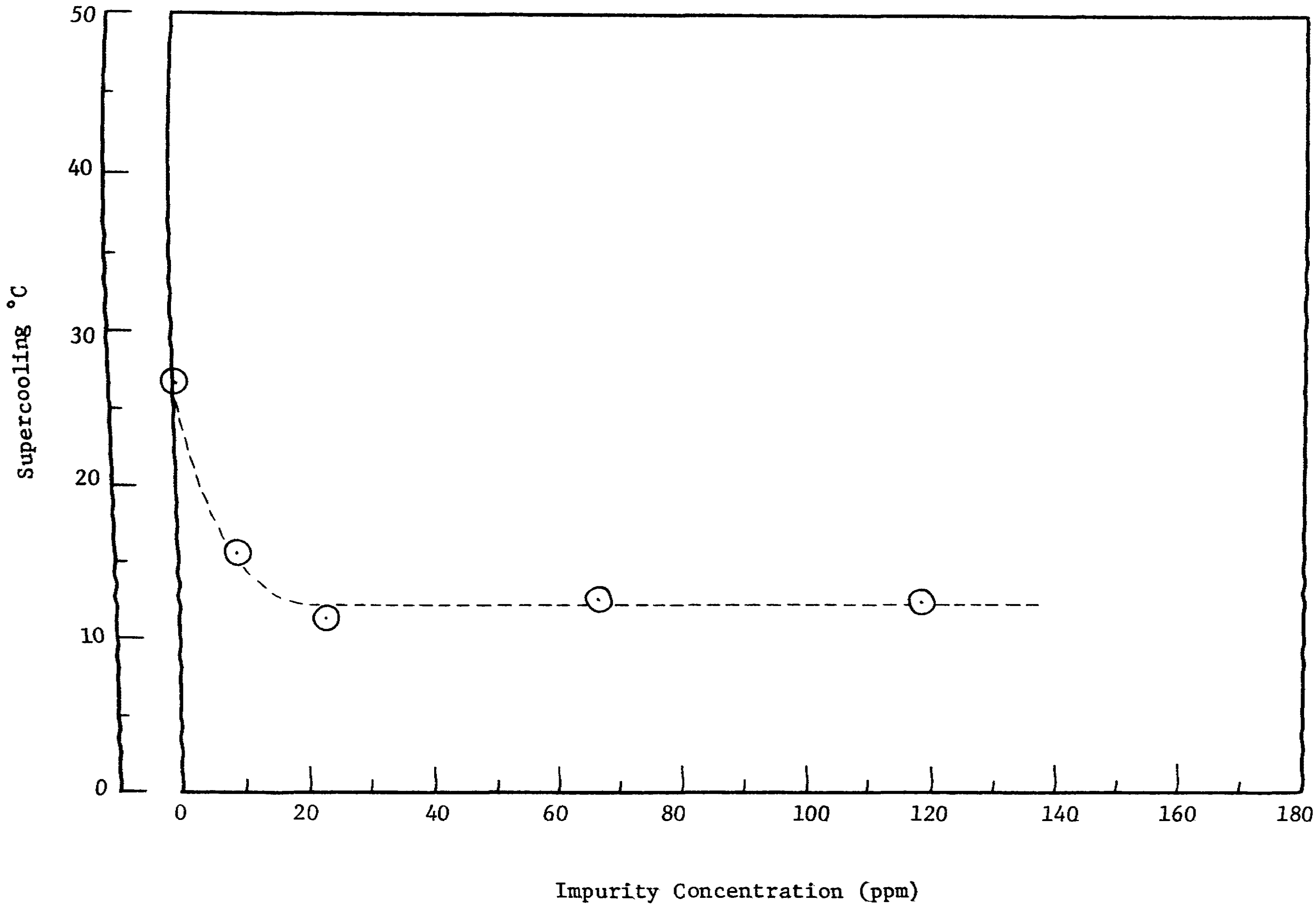


Figure 22. The Relationship Between Indium Concentration and The Supercooling Behavior of High-Purity Liquid Bismuth

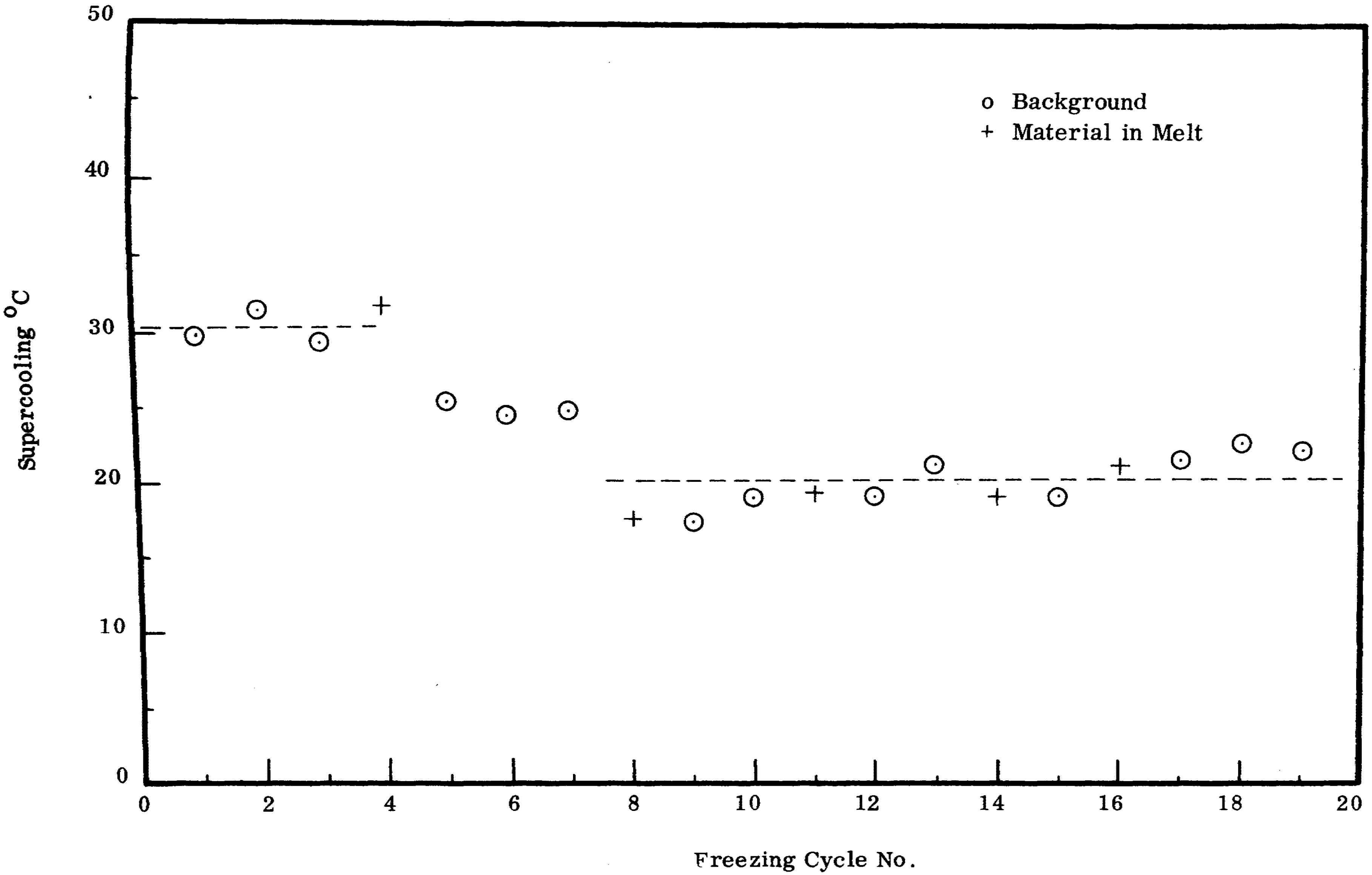


Figure 23. The Effect of Cadmium Additions on The Supercooling Behavior of Bismuth

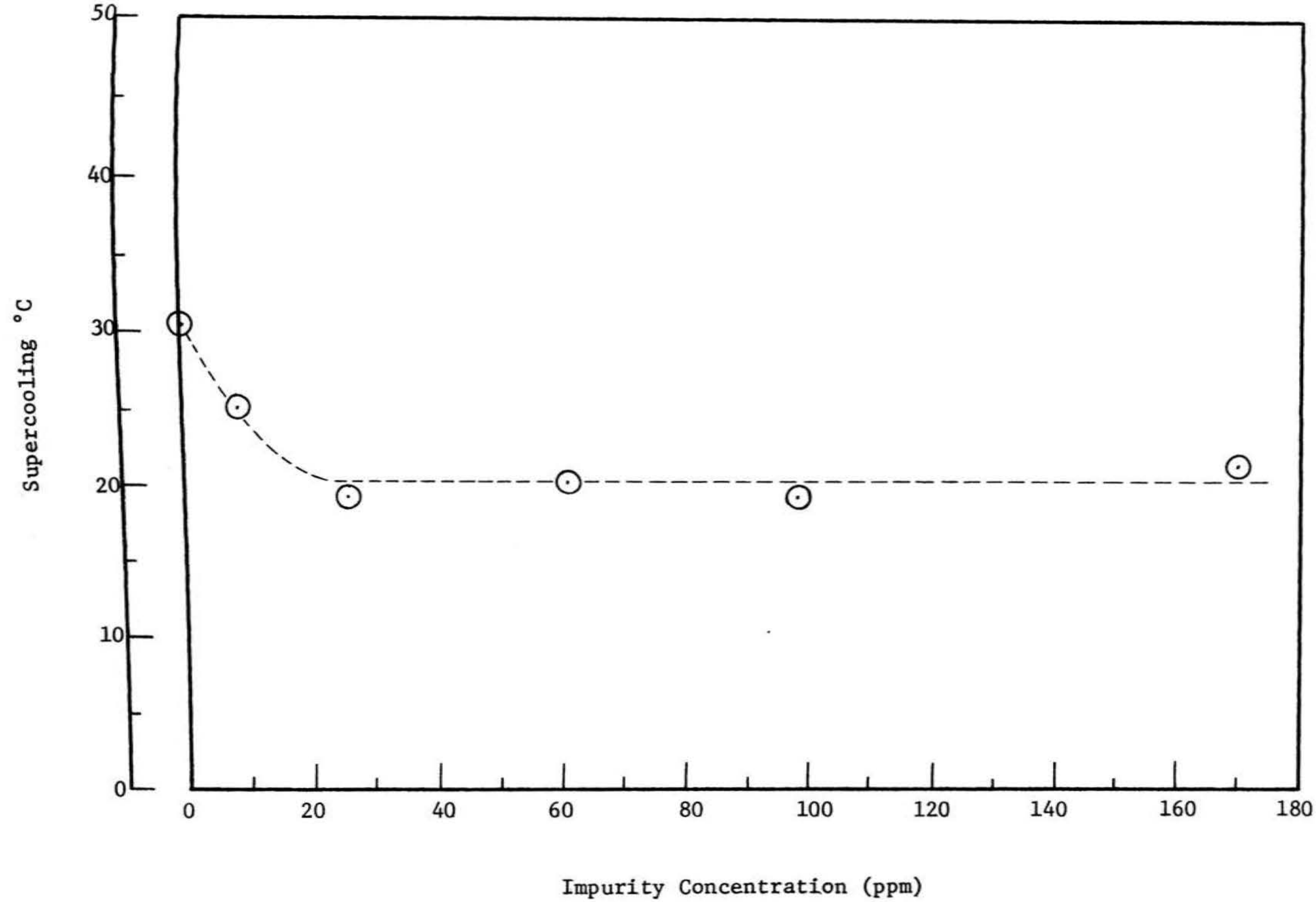


Figure 24. The Relationship Between Cadmium Concentration and The Super-cooling Behavior of High-Purity Liquid Bismuth

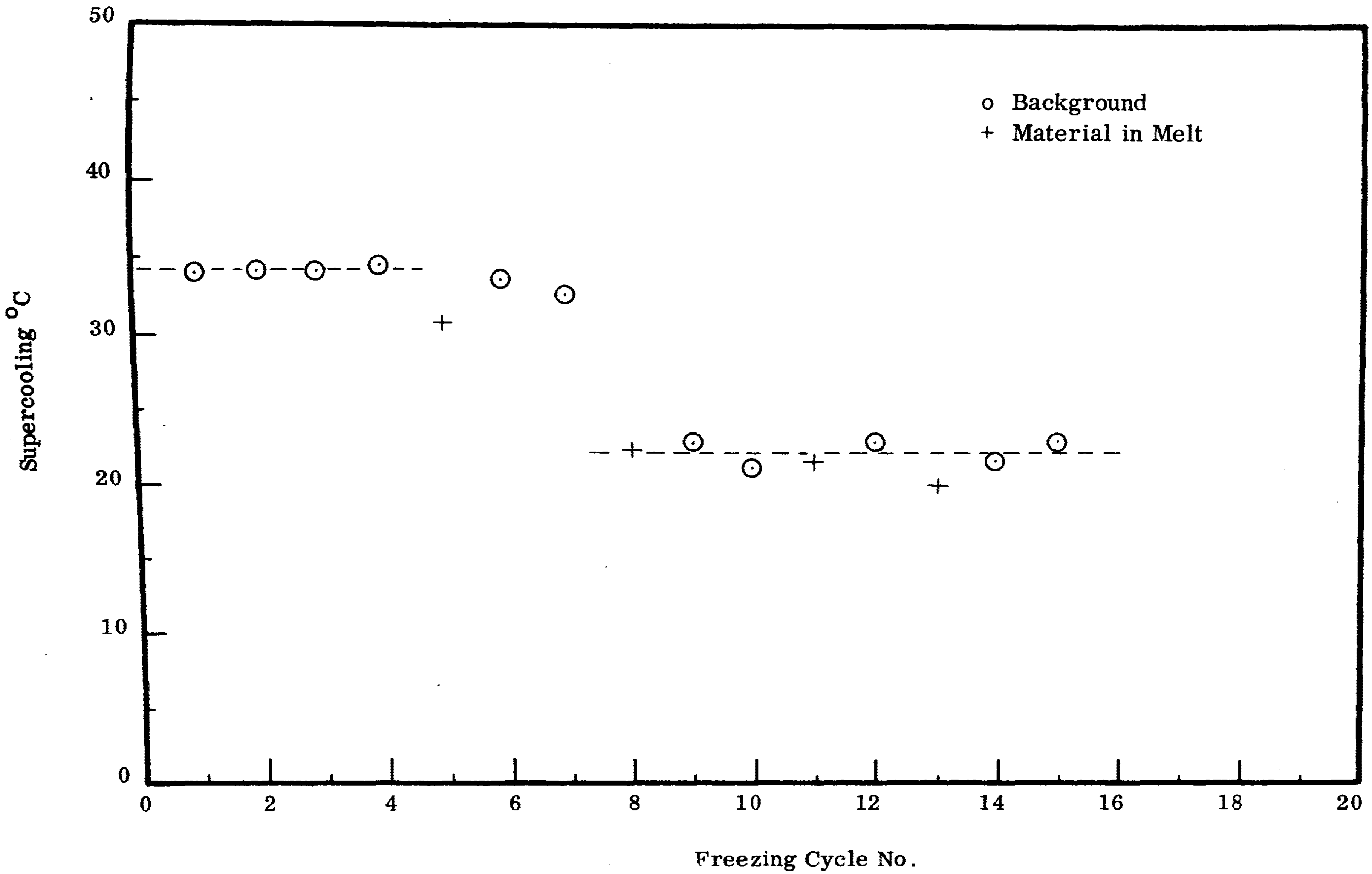


Figure 25. The Effect of Lead Additions on The Supercooling Behavior of Bismuth

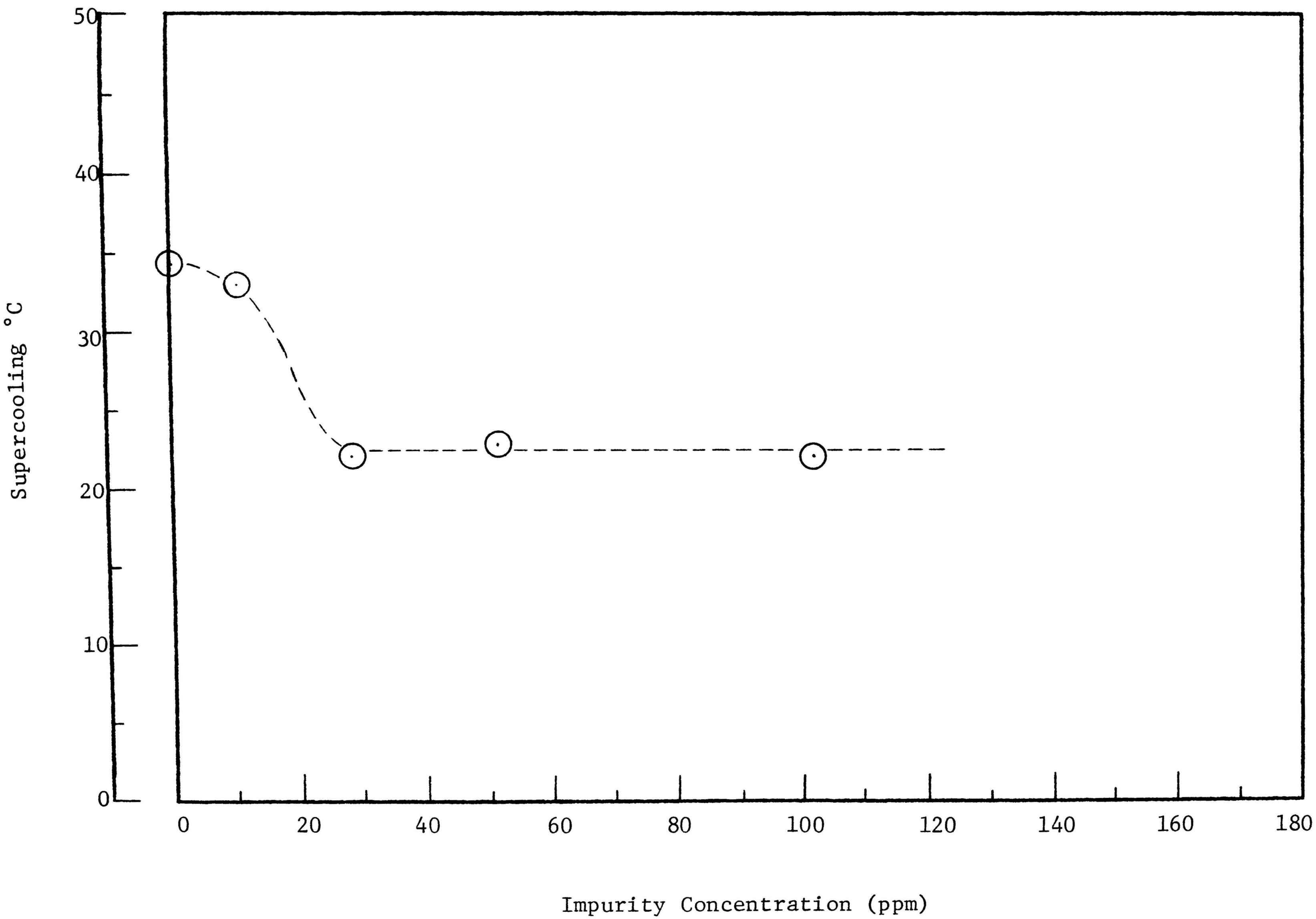


Figure 26. The Relationship Between Lead Concentration And The Supercooling Behavior of High-Purity Liquid Bismuth

addition of these metals to a pure bismuth melt gradually decreased the average background supercooling of pure bismuth. All of the previous elements caused a somewhat abrupt change when additions were made to the melt. The results for these metals can be seen in tables 13, 14 and 15 (Appendix) and figures 27, 28 and 29. All these plots show this gradual degradation of the supercooling behavior and they all seem to decrease the supercooling to a similar degree. A true characteristic supercooling value cannot be determined for these elements. The total amounts of gold, silver and copper added to a bismuth melt are 138.7, 110.7 and 23.0 ppm respectively.

Table 16 summarizes the characteristic supercooling data for those elements that had an effect on the supercooling behavior of pure bismuth. The elements are listed in the table in order of the most drastic (antimony) to the least effective (Cu, Ag, Au).

It may be noted from the above results that the average background supercooling of the bismuth before adding the foreign material varied in each case. It was found that this degree of variance had no effect on the characteristic supercooling value of the foreign material in the melt. The variance is probably due to the presence of a slight amount of oxide on the surface of the melt.

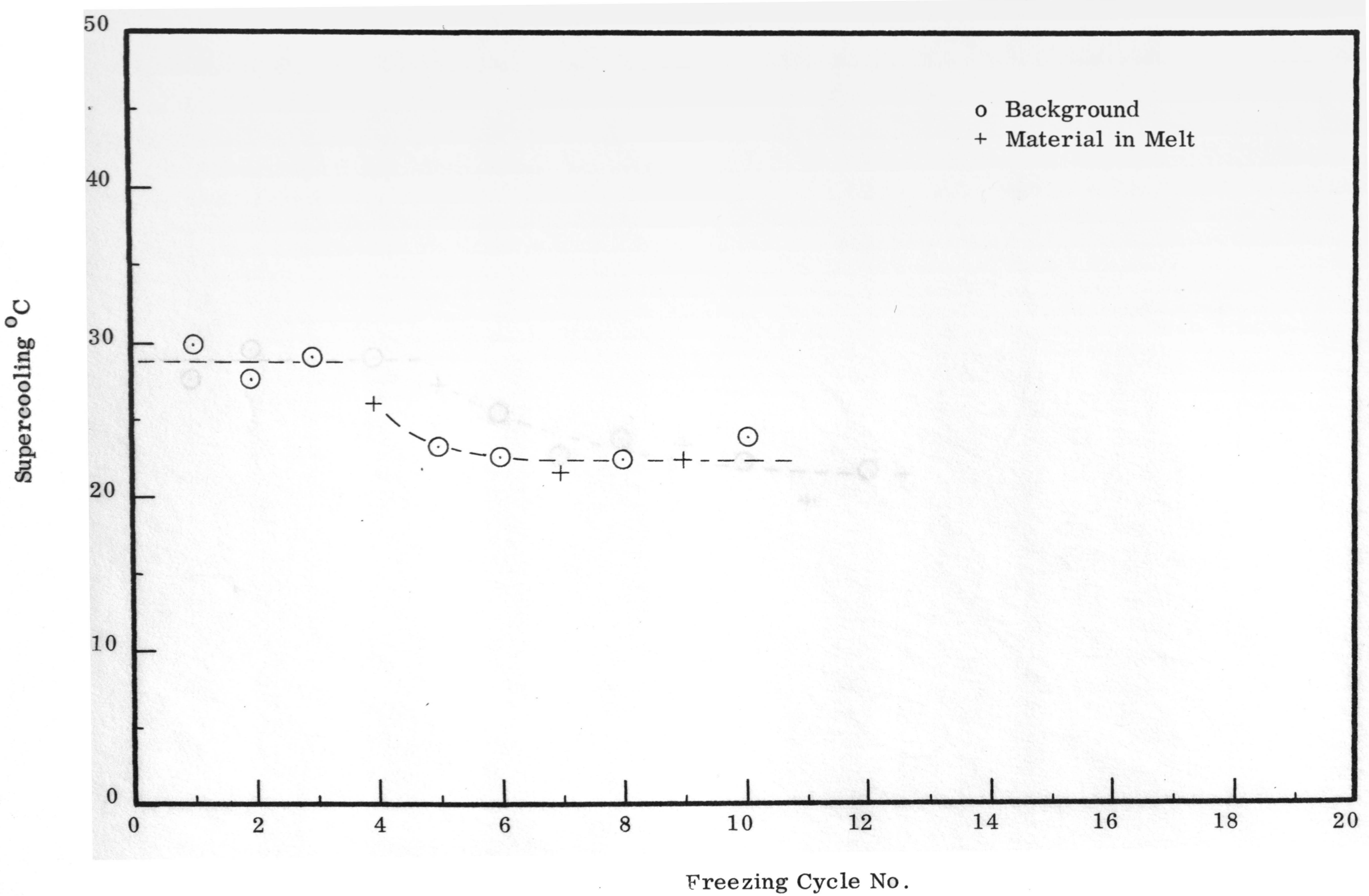


Figure 27. The Effect of Gold Additions on the Supercooling Behavior of Bismuth

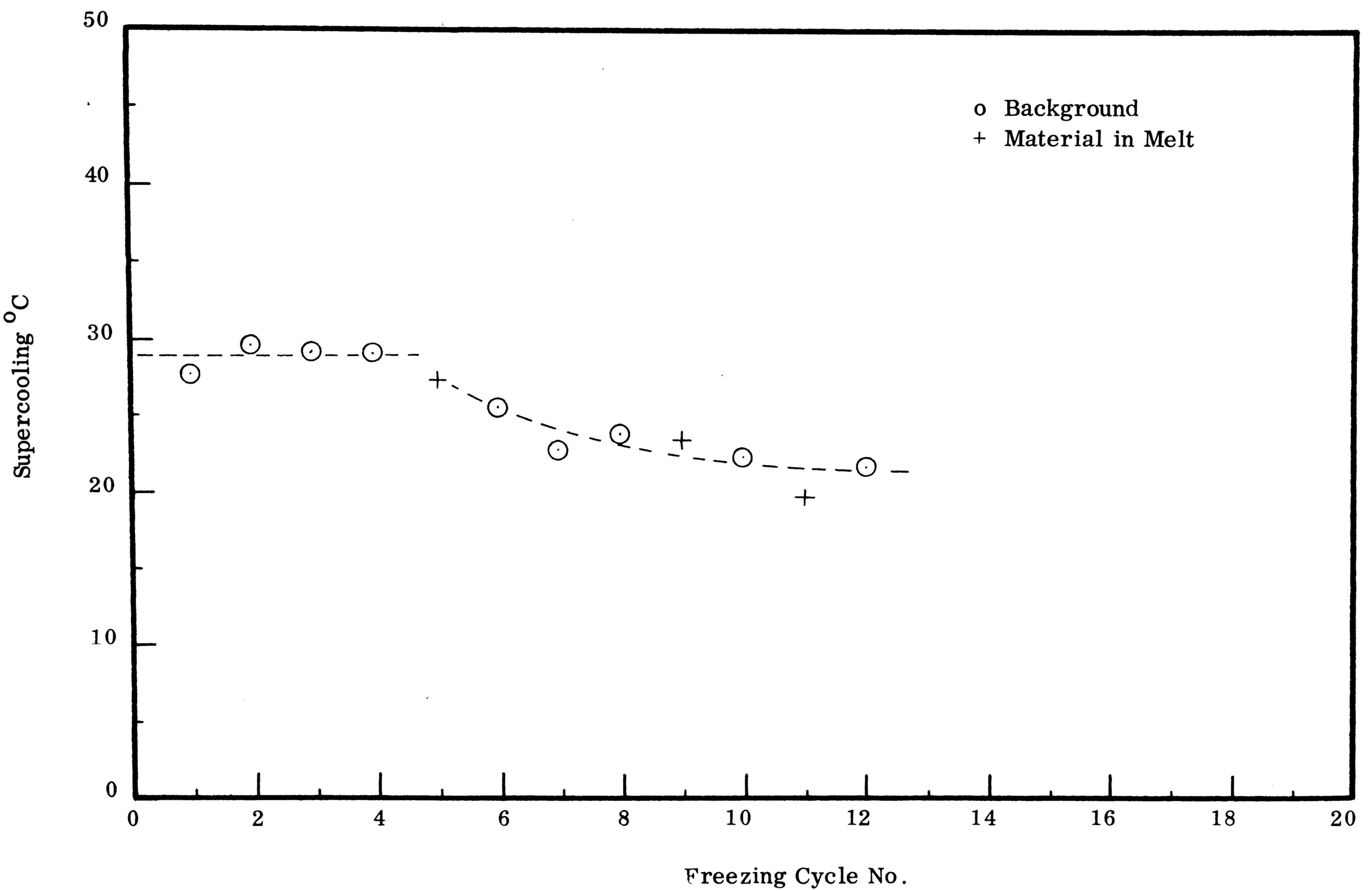


Figure 28. The Effect of Silver Additions on The Supercooling Behavior of Bismuth

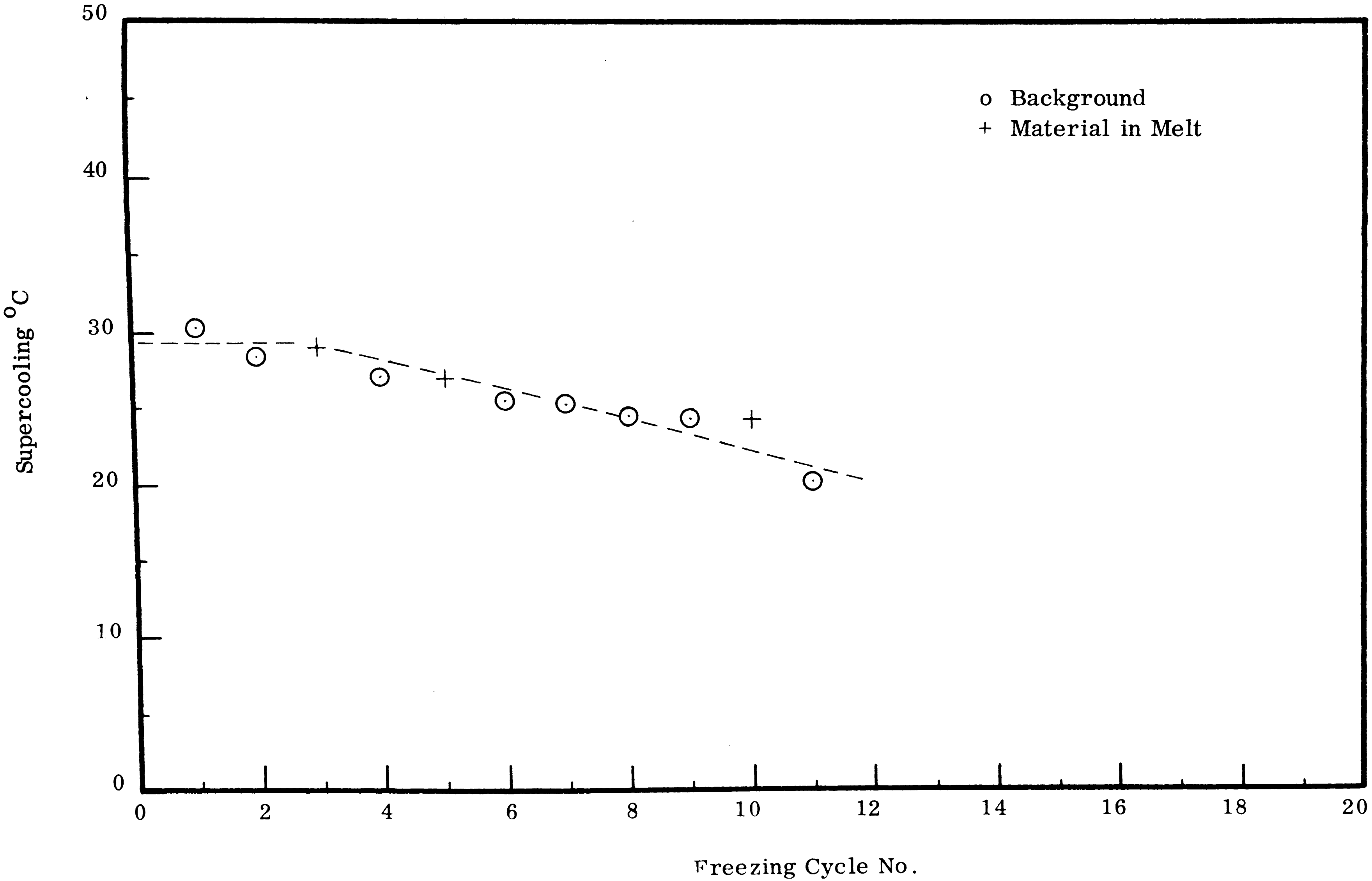


Figure 29. The Effect of Copper Additions On The Supercooling Behavior of Bismuth

TABLE 16

SUMMARY OF CHARACTERISTIC SUPERCOOLING DATA

Material Added To Melt	Characteristic Supercooling °C	Total Amount Added
Antimony	4.1	61.0 ppm
Tellurium	7.3	126.3 ppm
Indium	12.3	119.2 ppm
Selenium	14.2	152.0 ppm
Cadmium	20.4	199.6 ppm
Lead	22.4	102.0 ppm
Gold	*	138.7 ppm
Silver	*	110.7 ppm
Copper	*	23.0 ppm

*No Characteristic Supercooling Value Obtained.

V. DISCUSSION OF RESULTS

The discussion of results will be divided into 4 phases namely, Phase One - effect of melting atmosphere, Phase Two - the effect of superheat, Phase Three - the effect of non-metallic foreign materials and Phase Four - the effect of metallic foreign elements. Detailed consideration will be given to the latter phase since it constituted the bulk of the results of the investigation.

(A) Phase One - The Effect of Melting Atmosphere

The first phase of this investigation involved a study of the effect of the melting atmosphere on the supercooling behavior of high-purity liquid bismuth. As indicated by the results, the melting atmosphere plays an important role in the supercooling of bismuth. By melting in air a thick oxide surface film forms that restricts the supercooling to less than about 10°C while melting under a vacuum the supercooling is increased to about 25°C and by melting the bismuth under a hydrogen atmosphere the oxide surface film is chemically reduced and fairly high supercooling values on the order of 30 to 50°C are obtainable. Thus, the concentration of the bismuth oxide on the surface of the melt is a controlling factor in the supercooling behavior of pure bismuth. The bismuth oxide surface layer

can be considered as being similar to a surface-active substance which indicates the role surface-activity plays in supercooling phenomena. It is well known that oxide films can affect the surface tension values for liquids when compared with oxide free surfaces. The role of surface-active elements and surface oxide films will be taken up in a later section of this discussion.

(B) Phase Two - The Effect of Superheat

The second phase of the investigation was a study of the effect of superheat on the supercooling behavior of liquid bismuth. As can be seen from the results of this phase, the amount of superheat is only important when a thick oxide layer is present, as in air melting. For large amounts of superheat no effect is noted but when the superheat is below about 15°C the resulting supercooling is drastically reduced. This phenomenon has been known for a number of years[25] and is attributed[6][7] to the retention of solid nuclei of bismuth in the oxide surface layer that effectively promote nucleation upon cooling below the melting temperature. It is plausible that these small nuclei are not destroyed below about 15°C superheat.

(C) <u>Phase Three - The Effect of Non-Metallic Foreign Materials</u>

The third phase of the investigation involved a study of the effect of non-metallic foreign materials on the supercooling behavior of high-purity liquid bismuth. As can be seen from the results of this phase, none of the non-metallic materials altered the background supercooling of pure bismuth. It was observed that the liquid bismuth did not wet any of the non-metallic materials. For nucleation to take place, the melt must come into intimate contact with the catalyst or foreign material and form a coherent boundary between the catalyst and the nucleated solid(8). This type of contact was not observed to exist between the 12 non-metallic foreign materials and the bismuth melt. Bismuth oxide, which one would expect to have an effect as indicated in the first phase of the investigation, did not change the supercooling behavior. This may be attributed to the fact that bismuth oxide only affects the supercooling behavior if it has formed a natural layer on the melt surface and is wetted by the molten bismuth.

(D) <u>Phase Four - The Effect of Metallic Foreign Materials</u>

The last phase of the investigation was a study of the effect of metallic foreign materials on the

supercooling behavior of bismuth. It can be seen from the results that only 9 of the 28 metallic elements, listed in table 2, altered the supercooling behavior. These nine elements are antimony, tellurium, indium, selenium, cadmium, lead, gold, silver and copper. Some of the crystallographic and physical properties of these elements are listed in tables 17 and 18. Bismuth is included in the tables for a comparison of properties with the other elements. The elements are listed in decreasing order of effectiveness in altering the supercooling behavior of liquid bismuth. Most of the other 19 elements, listed in table 2, tried as nucleating agents were not "wetted" by the liquid bismuth and thus were not effective nucleating agents.

The elements antimony and tellurium when added in small quantities to the bismuth melt drastically reduced the degree of supercooling. As can be seen in the above tables, both these elements have similar properties to those of bismuth. Sundquist and Mondolfo[23], in their investigation of the supercooling behavior of a number of binary systems, concluded that, elements that are good nucleating agents have complex structures and high entropies of fusion. Thus, on this basis, antimony and tellurium can be predicted as being effective nucleating agents in liquid bismuth.

TABLE 17

CYRSTALLOGRAPHIC PROPERTIES OF THE ELEMENTS THAT AFFECTED THE SUPERCOOLING BEHAVIOR OF HIGH-PURITY LIQUID BISMUTH[40, 41]

Element	Crystal Structure	Lattice Spacing, Å a_o	Lattice Spacing, Å c_o	Atomic Diameter Å	Closest Approach Å	Goldschmidt Atomic Radii Å
Bismuth	Hex. (A7)	4.546	11.860	3.64	3.11	1.70
Antimony	Hex. (A7)	4.307	11.273	3.23	2.903	1.59
Tellurium	Hex. (A8)	4.45653	5.92682	3.40	2.87	1.60
Indium	Tetragonal	3.2517	4.9459	3.14	3.25	1.66
Selenium	Hex. (A8)	4.36397	4.65945	3.20	2.32	1.6
Cadmium	H.C.P. (A3)	2.9793	5.6181	3.04	2.979	1.52
Lead	F.C.C. (A1)	4.9495	-----	3.49	3.499	1.75
Gold	F.C.C. (A1)	4.0786	-----	2.88	2.884	1.44
Silver	F.C.C. (A1)	4.08621	-----	2.88	2.888	1.44
Copper	F.C.C. (A1)	3.6150	-----	2.55	2.556	1.28

PHYSICAL PROPERTIES OF THE ELEMENTS THAT AFFECTED THE SUPERCOOLING BEHAVIOR OF HIGH-PURITY LIQUID BISMUTH[41, 42]

Element	Melting Point, °K	Heat of Fusion K cal/g-atom	Entropy of Fusion K cal/g-atom/°K	Interfacial Energy (S-L) K cal/g-atom	Atomic Volume cm^3/g-atom
Bismuth	544	2.60	4.80	0.825	21.3
Antimony	903	4.74	5.25	1.430	18.4
Tellurium	723	4.18	5.80	-----	20.5
Indium	429	0.78	1.85	-----	15.7
Selenium	490	1.30	2.65	-----	16.5
Cadmium	594	1.45	2.45	-----	13.0
Lead	601	1.14	1.90	0.479	18.3
Gold	1336	2.95	2.20	1.320	10.2
Silver	1233	2.85	2.30	1.240	10.5
Copper	1357	3.12	2.30	1.360	7.1

But these factors seem to be of no significance when the nucleating agent is completely dissolved in the melt[39]. In the formal theory of heterogeneous nucleation a solid catalytic surface is necessary to promote nucleation. Since all the elements listed in table 18 are completely dissolved in the melt, the existing nucleation theory cannot be used to explain the results of this investigation.

It was also observed that some elements that dissolve in liquid bismuth do not effect the supercooling behavior, e.g. tin and palladium. A suitable explanation must therefore be proposed to describe the role of minor impurities in affecting supercooling behavior of a bismuth melt.

A possible approach to an explanation of this phenomena lies in a study of the change in the properties of liquid bismuth with small amounts of impurities. For years it has been known that certain minor impurities can drastically effect the surface tension of liquids. For example, potassium can change the surface tension of liquid bismuth from 375 dynes/cm to about 340 dynes/cm in a concentration of 0.025 atomic percent[43]. Tellurium has a similar effect in that it can reduce the surface tension of liquid bismuth to about 350 dynes/cm when added in concentrations of about 0.25 atomic percent[44].

The decrease in surface tension is attributed to the adsorption of these elements on the surface of the liquid. If a substance is adsorbed on the surface of a liquid it is said to be "surface active" and if it is distributed throughout the bulk of the liquid it is said to be "surface inactive". Since these are pronounced changes in the properties of a liquid with minor impurities, they may be a clue to the changes in supercooling experienced in this investigation.

Data on surface active and surface inactive elements in liquid bismuth[45], indicate that tellurium is a surface active element. Thus, tellurium being surface active, reduces the surface tension of bismuth as indicated above, and drastically reduces the supercooling behavior of liquid bismuth as determined by this investigation at about the same concentration level. The element tin is known to be surface inactive and does not alter the supercooling behavior of liquid bismuth. These data seem to indicate the role surface activity plays with changes in supercooling behavior, but a definite correlation cannot be established unless data are known about the other elements used in this investigation. Unfortunately data of this nature are scarce so that predictions must be made as to the surface active nature of these elements.

(1) Theoretical Aspects of Surface Activity in Liquid Metals

Semenchenko[45] presented a theory from which predictions can be made for determining the surface active or surface inactive nature of various elements in liquid metals. He bases these predictions on the difference in the "generalized moments" of the solvent (bismuth) and the dissolved element (antimony, tellurium, etc.). The generalized moment is defined as an energy characteristic expressing the energetic properties of an ion. The equation for the generalized moment, m, is:

$$m = \frac{e\ Z}{r}$$

Where:

e = Charge of the electron (4.8×10^{-10} esu)

Z = Valence of the ion

r = Effective radius of the ion.

The expression holds for both ionic and metallic liquids. The generalized moment can be used to predict the behavior of an element with regard to compressibility, surface tension, surface activity, and many thermodynamic properties. According to Semenchenko, all elements with generalized moments less than the generalized moment of the solvent

are surface active and those elements having larger moments are surface inactive. Thus, the larger the positive difference in the generalized moments the greater the surface activity and the larger the negative difference the greater the surface inactivity.

(2) Application of The Theory of Surface Activity To Materials Studied in This Investigation

The equation for the generalized moment can then be applied to the materials studied in the present investigation. Difficulty arises in assigning a definite valence and ionic radius to liquid bismuth since bismuth ions can exist with charges of +3, +5 and -3. Semenchenko, in his use of the equation for metallic liquids, uses the lowest valence state of the element. Thus, bismuth with a -3 valence has an ionic radius of 2.3 Å[46] and thus a generalized moment of 6.67×10^{-2} esu (absolute value). The calculated generalized moments for the dissolved elements can be found in table 19 along with the data for bismuth. The elements are listed in order of decreasing effectiveness. It is evident from these calculations that the elements, tellurium, selenium, gold, silver and copper are surface active and that antimony, indium, cadmium, and lead are surface inactive. The elements tellurium and

TABLE 19

CALCULATED GENERALIZED MOMENTS FOR THE ELEMENTS THAT AFFECTED THE SUPERCOOLING BEHAVIOR OF BISMUTH

Element	Ionic Valence	Ionic[46] Radius, Å	Generalized Moment, esu	Difference in Moments (m_{Bi} - M_x)
Bismuth	-3	2.13	6.67×10^{-2}	-----
Antimony	-3	2.08	6.92×10^{-2}	-0.16
Tellurium	-2	2.11	4.55×10^{-2}	+2.21
Indium	+3	0.92	15.66×10^{-2}	-8.90
Selenium	-2	1.93	4.97×10^{-2}	+1.79
Cadmium	+2	0.99	9.70×10^{-2}	-1.94
Lead	+2	1.26	7.62×10^{-2}	-0.92
Gold	+1	1.37	3.51×10^{-2}	+3.25
Silver	+1	1.13	4.25×10^{-2}	+2.25
Copper	+1	0.98	4.90×10^{-2}	+1.86

selenium, with differences in generalized moments of +2.21 and +1.79, respectively, indicate that tellurium is more surface active than selenium and also has a greater effect on supercooling. According to this trend, the elements, gold, silver, and copper should have smaller differences in generalized moments than selenium due to their slight effect on supercooling as shown in table 16. As can be seen from table 19, these elements do not seem to follow this trend. This can be attributed to the vast difference in properties between these face-centered cubic metals and those of bismuth. This aspect will be taken up in a later section of the discussion.

Since the elements tin and palladium also dissolved in the bismuth melt the theory of Semenchenko should be applied to these elements. The calculated generalized moment for tin is 9.4×10^{-2} esu and for palladium is 30×10^{-2} esu. Both these elements have generalized moments greater than bismuth and are thus considered as being surface inactive. It should also be noted that these elements had no effect on the supercooling behavior of bismuth.

(3) The Role of Oxide Films on The Melt Surface

As mentioned above, the elements antimony, indium, cadmium and lead are considered surface inactive according

to the theory of Semenchenko. These elements may be concentrated on the melt surface in the form of an oxide since these elements are capable of reducing bismuth oxide according to simple thermodynamic calculations. These calculations are given in the appendix. Thermodynamic calculations can also show that tellurium, selenium, gold, silver and copper are incapable of reducing bismuth oxide at these low temperatures. Thus, these elements are concentrated on the melt surface due to their surface active nature.

The formation of oxides of antimony, indium, cadmium and lead requires the presence of bismuth oxide or oxygen at the surface of the melt or beneath the melt surface. It is plausible to expect some bismuth oxide to be present since the supercooling of the pure bismuth melt is limited to about 50°C. Other investigators[32,33,34] using various fluxes on the melt surface have obtained supercoolings in excess of 90°C. These fluxes tend to absorb any impurities, such as bismuth oxide, and render them ineffective in promoting nucleation. Since fluxes were not used in the present investigation some bismuth oxide may still be present even though the bismuth was melted under a hydrogen atmosphere. Some bismuth oxide exists along the crucible-melt surface

that is essentially not affected by the hydrogen atmosphere. This oxide may be reduced by the surface inactive elements dissolved in the melt and tie-up these elements on the surface.

(4) A Mechanism for The Nucleation of Bismuth by Impurities Concentrated on The Melt Surface

Since the dissolved elements listed in table 19 affected the supercooling behavior of high purity liquid bismuth, a relationship must be established to relate the concentration of impurities on the melt surface to changes in supercooling behavior. Since the impurities can be concentrated on the melt surface in elemental form (surface active) or in the form of an oxide layer this section will be divided into two units.

(a) The Surface Active Elements

Russian investigators[48] have found that potassium, a surface active substance in liquid mercury, will decrease the supercooling of pure mercury and similar results have been found with magnesium additions in steel[49]. A suitable explanation has not been proposed for this phenomenon.

An explanation for this decrease in supercooling, caused by the addition of small quantities of surface active

elements such as tellurium can be deduced as follows. These elements tend to concentrate on the surface of the bismuth melt, thus forming a layer of atoms that acts as a site for heterogeneous nucleation. This layer is essentially a sheet of atoms that simulates a solid catalytic surface. By a number of assumptions one can calculate the approximate number of atoms necessary to form a monolayer on the melt surface used in this investigation. The approximate surface area of the exposed melt surface is 5 cm^2 and by assuming that each atom has a diameter of about 3 Å it would require about 10^{16} atoms to form a complete monolayer. In the case of tellurium it required an addition of about 0.25 mg (about 4 ppm) or about 10^{18} atoms to produce the characteristic supercooling value of 7.3°C. Thus, from this rough calculation it is possible to form a complete monolayer at the melt surface with these small concentrations of impurities.

Figure 30 shows the proposed idealized model for the nucleation of a cluster of bismuth atoms by a monolayer on the melt surface. A monolayer is assumed for simplicity of the proposed model although layers thicker than one atomic diameter are also possible with the same effectiveness in nucleation. The atomic packing of the monolayer

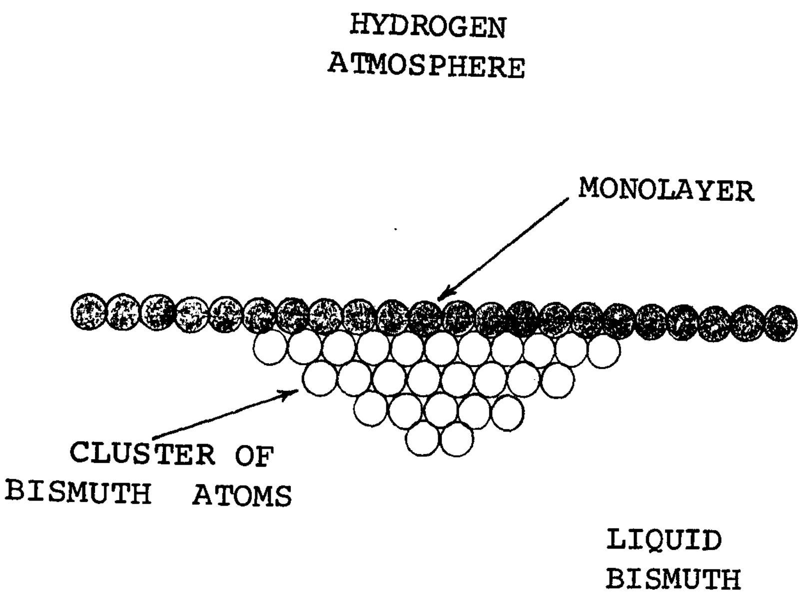
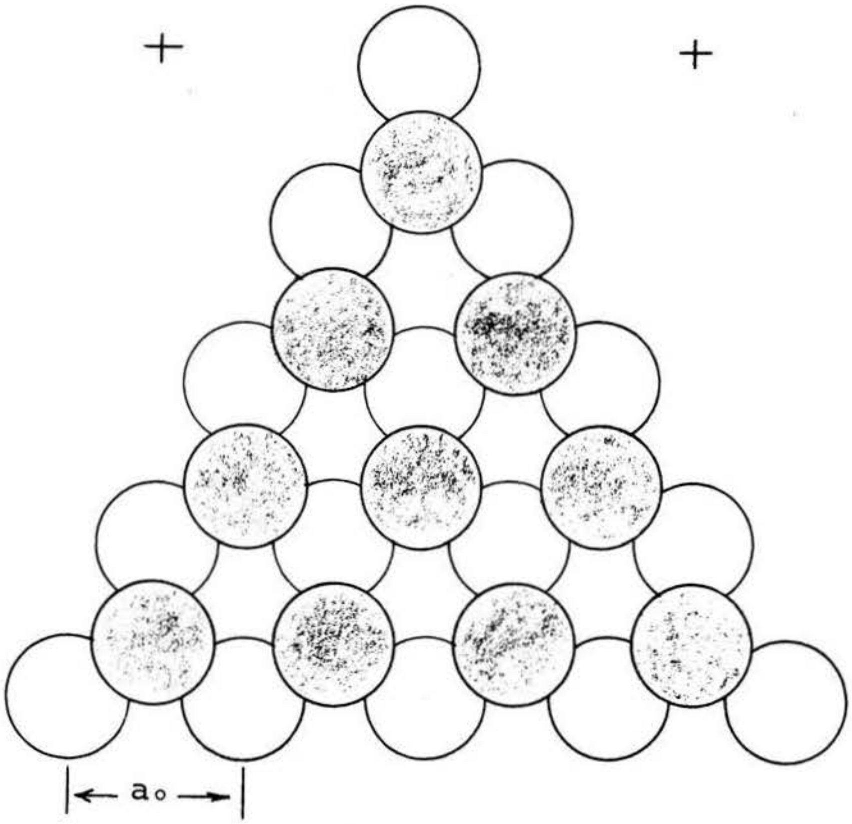


Figure 30. Nucleation of A Cluster of Bismuth Atoms By A Monolayer of Foreign Atoms On The Melt Surface.

simulates a 2-dimentional crystal or plane of atoms. Although the atomic packing of atoms in the liquid state is of a somewhat random nature, the packing of atoms in a surface monolayer may assume a more ordered pattern since the atoms are forced into a two dimensional array. Thus, the monolayer can consist of islands or "grains" of an ordered array of atoms. The degree of order and the coherency between the monolayer and the cluster of bismuth atoms, as shown in figure 30, determines the ease at which nucleation can take place as proposed in an earlier theory by Turnbull and Vonnegut[8]. This theory, which was substantiated by previous investigations[30][35], will be used in discussing the relationship between the monolayer and the nucleated bismuth cluster. The better the coherency between the monolayer surface and the surface of the bismuth cluster, the less the degree of supercooling of the melt. Thus, tellurium having similar crystallographic characteristics to those of bismuth would act as a good nucleating agent and require a small degree of supercooling. A glance at table 17 will indicate that as the degree of supercooling increases the crystallographic properties differ more and more from those of bismuth.

To establish the nature of the coherency between the monolayer, of the surface active elements, and the cluster of bismuth atoms, the crystallographic planes of both phases must be known. For example, it is known that the preferred growth direction for bismuth is the $\langle 111 \rangle$ perpendicular to the $\{111\}$[50]. The (111) is essentially a fairly close packed hexagonal array of atoms, as shown in figure 31. The shaded atoms can be located either above or below the (111) so that each atom has three nearest neighbors. The atomic radius of 1.55 Å was calculated from the Goldschmidt radius by assuming a 15% reduction in transforming from a coordination number of twelve to a coordination number of three. The Goldschmidt radii for a coordination number of twelve are given in table 17. The interatomic spacing, a_o, is given as 4.546 Å and is indicated on figure 31. This plane of atoms is assumed to be the plane which must be established for heterogeneous nucleation of bismuth to take place.

The crystallographic relationships of the proposed monolayers of the surface active elements tellurium, selenium, gold, silver and copper are given in the appendix in the form of transparencies or overlays. These overlays which which are drawn to the same scale, can be placed directly over the (111) of bismuth shown in figure 31, by the proper



Scale: 1cm = 2Å

$a_\circ = 4.546$ Å

Figure 31. The (111) of Bismuth Showing the Location of Atoms

matching of the fiduciary marks, to show the degree of coherency between the two structures. For example, the (001) of tellurium when placed in the proper position over the (111) of bismuth shows a high degree of coherency between the two planes thus indicating that tellurium should be a good nucleating agent for bismuth. The selenium (001) shows a lower degree of coherency indicating that it is not as effective as tellurium as a nucleating agent. This trend was observed in the experimental results as listed in table 16. Since the interatomic spacings for tellurium and selenium are 4.45645 Å and 4.36397 Å respectively, one can calculate the lattice disregistry factors using the Turnbull-Vonnegut equation(8):

$$\delta = \frac{\Delta a}{a_o}$$

Where:

δ = The disregistry factor

Δa = The difference between the lattice spacing of bismuth and the catalyst

a_o = The lattice spacing of bismuth

The disregistry factor for tellurium was calculated as 0.019 and for selenium as 0.040. The smaller the disregistry factor the greater the coherency between the bismuth cluster and the monolayer and the lower the degree of supercooling required for nucleation to take place.

The (111) of gold and silver does not closely match the (111) of bismuth thus these elements should have little effect on the supercooling behavior of bismuth. This was observed from the experimental results of this investigation. The (111) of copper is similar to the (111) of gold and silver except for its smaller atomic diameter. The interatomic spacing for gold and silver is 2.88 Å and for copper is 2.55 Å. The disregistry factors for these elements are calculated as: 0.366 for gold and silver and 0.439 for copper. As can be seen, these factors are much greater than those calculated for tellurium and selenium.

From the above reasoning, the surface active elements follow a definite trend in their effect on the supercooling behavior of bismuth. The closer the match between the crystallographic plane of the surface layer and the (111) of bismuth the greater the effect on the supercooling of bismuth.

(b) <u>The Oxide Forming Elements</u>

If some of the impurity elements are tied up in the form of an oxide surface monolayer, the above data cannot be considered since the oxides have different properties than the pure elements. Niwa et. al.[47] have

determined the orientation and structure of oxide films formed on a melt surface. These data are listed in table 20 for a number of oxides of interest to this investigation. As can be seen from these data, the oxides of bismuth, antimony and indium have similar crystallographic properties. Bismuth oxide, Bi_2O_3, exists as a (pseudocubic) tetragonal structure[51] with $a_o = 10.95$ Å, and In_2O_3 exists as a cubic structure with $a_o = 10.118$ Å. It is evident that a surface oxide film can effect the supercooling of bismuth as shown by the results of the first phase of this investigation; thus, if antimony, indium, lead and cadmium are on the surface in the form of oxide film, they may also effect the supercooling behavior similar to bismuth oxide.

The crystallographic relationships for the oxide films can be compared with the crystallographic relationship of the (111) of bismuth shown in figure 31. The (111) of antimony oxide, Sb_2O_3, has been constructed in the form of an overlay found in the appendix. The large circles represent oxygen and the smaller circles represent antimony with ionic radii of 1.40 Å for O^{-2} and 0.76 Å for Sb^{+3}. The scale is the same as the (111) of bismuth and the interatomic spacing between oxygen atoms is 7.8 Å. By proper matching of the fiduciary marks one can see the close

TABLE 20

ORIENTATION RELATIONSHIPS OF OXIDES FORMED ON THE SURFACE OF A MELT[47][51]

Oxide	Crystal Structure	Lattice Spacing, Å a_o	b_o	c_o	Orientation of Oxide Film	
Bi_2O_3	Tetragonal	10.95	-----	5.63	(221)	Melt Surface
Sb_2O_3	Cubic (ZnS)	11.152	-----	-----	(111)	Melt Surface
Sb_2O_4*	Orthorhombic	4.814	5.435	11.78	(111)	Melt Surface
In_2O_3	Cubic (B.C.)	10.118	-----	-----	Unknown	
CdO	Cubic (NaCl)	4.6953	-----	-----	(001)	Melt Surface
PbO	Orthorhombic	7.79	5.50	7.65	(001)	Melt Surface
PbO*	Tetragonal	3.9729	-----	5.0192	(001)	Melt Surface
SnO_2	Tetragonal(TiO_2)	4.737	-----	3.185	(101)	Melt Surface
SnO	Tetragonal(PbO)	3.802	-----	4.836	(001)	Melt Surface

* Small quantity contained in surface layer

coherency between the two planes, indicating that antimony oxide should be a very effective nucleating agent for bismuth. The interatomic distance between an oxygen atom and an antimony atom is 4.503 Å, thus yielding a disregistry value of 0.0094.

This disregistry factor is less than the factor calculated for tellurium indicating that antimony oxide is more effective than tellurium as a nucleating agent. The same trend was observed in the results of this investigation listed in table 16.

An overlay was constructed for cadmium oxide, CdO, since its structure (NaCl) is well established. As can be seen from this overlay, the matching of the (001) of CdO with the (111) of bismuth is not close. Therefore this oxide is not as effective as antimony oxide as a nucleating agent for bismuth. The oxides of indium and lead, are not drawn due to uncertainties in their exact structure.

Table 20 includes data for tin oxide surface films, since tin dissolved in liquid bismuth and was found to be surface inactive. The properties of this oxide differ from the properties of bismuth, antimony and indium oxides to the extent that the oxide has essentially no effect in

promoting nucleation of bismuth. Two forms of tin oxide are given since both seem to form surface layers on a tin melt. The other element, palladium, which dissolved in liquid bismuth and had no effect on the supercooling does not form an oxide at these low temperatures.

To summarize the disregistry factors for some of the impurity elements that altered the supercooling of bismuth, table 21 has been included. The calculated disregistry values follow a definite trend with regard to the effect of these elements on the supercooling of bismuth. The smaller the disregistry factor the closer the fit between the plane of the impurity layer and the (111) of bismuth thus yielding a smaller degree of supercooling. These data, as tabulated in table 21, lend definite support to the Turnbull-Vonnegut theory proposed a number of years ago.

TABLE 21

SUMMARY OF DISREGISTRY FACTORS FOR SOME OF THE ELEMENTS THAT ALTERED THE SUPERCOOLING OF BISMUTH

Element	Characteristic Supercooling, °C	Disregistry Factor
Antimony (Oxide)	4.1	0.009
Tellurium	7.3	0.019
Selenium	14.2	0.040
Cadmium (Oxide)	20.4	0.231
Gold	Greater than 20°C	0.366
Silver	Greater than 20°C	0.366
Copper	Greater than 20°C	0.439

VI. SUMMARY OF THE DISCUSSION OF RESULTS

It was observed that the supercooling behavior of high purity liquid bismuth was affected by a bismuth oxide surface layer and by the addition of minor impurities to the melt. It was proposed that the decrease in supercooling was due to the concentration of the elements or an oxide film on the surface. The elements can be concentrated on the surface of the liquid bismuth if they are surface active. Elements that affected the supercooling such as Te, Se, Ag Cu, Au, were determined as being surface active thus existing essentially in elemental form on the melt surface. The other impurity elements that affected the supercooling behavior such as Sb, In, Cd, and Pb were calculated to be surface inactive. These elements can be concentrated on the melt surface in the form of oxide films.

A mechanism was proposed whereby bismuth could nucleate heterogeneously on the surface of a monolayer of impurity atoms. If the elements were concentrated on the surface in elemental form, the crystallographic similarity of the monolayer structure to bismuth would determine the nucleation behavior. If the impurities were tied up in the form of an oxide the crystallographic plane of the oxide, exposed to the melt surface would be the controlling factor in

promoting heterogeneous nucleation. It was shown that those elements that had the greatest effect in decreasing the supercooling of bismuth were crystallographically similar in either elemental or oxide form. This substantiates the theory of Turnbull and Vonnegut with regard to lattice disregistry between the catalyst and the nucleated solid.

VII. CONCLUSIONS

The experimental evidence presented in this dissertation indicated that:

(1) The amount of bismuth oxide on the surface of a pure bismuth melt is a controlling factor in the amount of supercooling obtainable.

(2) With a thick surface oxide film present, a superheat below about 15°C will drastically decrease the amount of supercooling in pure bismuth whereas in the absence of the surface oxide film the amount of superheat is of no significance to the supercooling behavior.

(3) Elements such as tellurium, selenium, gold, silver and copper that dissolve in liquid bismuth and tend to concentrate on the melt surface can decrease the supercooling of bismuth depending upon the degree of coherency between the surface layer (monolayer) formed and the (111) of bismuth. These elements are surface active in liquid bismuth.

(4) Elements such as antimony, indium, cadmium and lead, that dissolve in liquid bismuth and form

a surface oxide film can decrease the supercooling of bismuth depending upon the coherency between the crystallographic plane of the oxide film and the (111) of bismuth.

(5) Surface active elements or oxide films, since they concentrate on the melt surface as a layer, act as a site for heterogeneous nucleation lending support to the Turnbull and Vonnegut disregistry theory.

VIII. RECOMMENDATIONS FOR FURTHER STUDY

A better understanding of the relationship between changes in supercooling and changes in the liquid state due to minor impurities should be explored. It should be possible to obtain data on the change in surface tension with small additions of the impurities studied in the present investigation. Once this data is made available it may be possible to obtain a direct relationship between changes in surface tension and supercooling. The same data would tend to prove or disprove the theory of Semenchenko with regard to surface activity for the elements studied in this investigation.

Experiments related to the study of oxide films on a bismuth melt should be undertaken. For example, a study of the effect of various H_2/H_2O ratios in controlling the concentration of bismuth oxide on the melt surface would be an important step into the understanding of the supercooling behavior of bismuth. The use of fluxes should also be investigated to see if the same results are obtained as in the present investigation, with regard to the role of minor impurities.

Melts other than bismuth should also be studied in a similar manner so that the data obtained can substantiate

the results of the present investigation. Melts of gallium, antimony, tin, etc. have never been studied from the viewpoint of the effect of minor impurities in decreasing the supercooling.

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APPENDIX

TABLE 5

THE EFFECT OF BORON CARBIDE ON THE SUPERCOOLING BEHAVIOR OF BISMUTH

Freezing Cycle No.	Supercooling °C	Condition
1	33.6	Background
2	33.6	B_4C in Melt
3	33.9	B_4C in Melt
4	33.6	B_4C in Melt
5	33.6	Background
6	33.6	Background

TABLE 6

THE EFFECT OF TIN ADDITIONS ON THE SUPERCOOLING BEHAVIOR OF BISMUTH

Freezing Cycle No.	Supercooling °C	Condition
1	27.2	Background
2	26.6	Background
3	29.4	Background
4	26.2	Background
5	23.0	16.9 ppm Sn Added
6	28.2	Background
7	28.2	Background
8	27.2	22.1 ppm Sn Added
9	28.8	Background
10	28.2	Background
11	28.8	41.7 ppm Sn Added
12	26.2	Background
13	30.0	Background
14	28.5	71.5 ppm Sn Added
15	30.7	Background

TABLE 7

THE EFFECT OF ANTIMONY ADDITIONS ON THE SUPERCOOLING BEHAVIOR OF BISMUTH

Freezing Cycle No.	Supercooling °C	Condition
1	37.1	Background
2	35.8	Background
3	36.5	Background
4	11.2	3.2 ppm Sb Added
5	14.1	Background
6	9.3	Background
7	4.5	6.3 ppm Sb Added
8	4.2	Background
9	5.1	12.9 ppm Sb Added
10	3.2	Background
11	4.5	Background
12	5.4	Background
13	3.8	16.6 ppm Sb Added
14	4.2	Background
15	3.8	22.1 ppm Sb Added
16	3.8	Background
17	3.8	Background

TABLE 8

THE EFFECT OF TELLURIUM ADDITIONS ON THE SUPERCOOLING BEHAVIOR OF BISMUTH

Freezing Cycle No.	Supercooling °C	Condition
1	42.9	Background
2	40.6	Background
3	9.6	3.9 ppm Te Added
4	10.6	Background
5	10.6	Background
6	7.7	10.2 ppm Te Added
7	8.0	Background
8	7.7	Background
9	6.7	28.6 ppm Te Added
10	7.0	Background
11	8.0	Background
12	7.0	40.2 ppm Te Added
13	7.7	Background
14	6.7	43.4 ppm Te Added
15	6.7	Background
16	6.4	Background
17	7.0	Background

TABLE 9

THE EFFECT OF INDIUM ADDITIONS ON THE SUPERCOOLING BEHAVIOR OF BISMUTH

Freezing Cycle No.	Supercooling °C	Condition
1	26.6	Background
2	26.9	Background
3	27.2	Background
4	22.4	9.2 ppm In Added
5	24.6	Background
6	17.3	Background
7	11.8	Background
8	14.1	Background
9	10.6	Background
10	10.2	16.2 ppm In Added
11	11.2	Background
12	12.2	Background
13	11.2	Background
14	8.3	41.7 ppm In Added
15	12.8	Background
16	12.8	Background
17	13.2	52.2 ppm In Added
18	12.5	Background
19	12.5	Background

TABLE 10

THE EFFECT OF SELENIUM ADDITIONS ON THE SUPERCOOLING BEHAVIOR OF BISMUTH

Freezing Cycle No.	Supercooling °C	Condition
1	28.1	Background
2	29.8	Background
3	30.0	Background
4	28.2	Background
5	7.7	50.6 ppm Se Added
6	15.0	Background
7	12.2	Background
8	9.6	101.4 ppm Se Added
9	13.1	Background
10	15.0	Background
11	14.7	Background
12	15.0	Background
13	14.7	Background

TABLE 11

THE EFFECT OF CADMIUM ADDITIONS ON THE SUPERCOOLING BEHAVIOR OF BISMUTH

Freezing Cycle No.	Supercooling °C	Condition
1	30.0	Background
2	31.7	Background
3	29.4	Background
4	31.0	8.9 ppm Cd Added
5	25.6	Background
6	24.6	Background
7	25.0	Background
8	17.9	18.1 ppm Cd Added
9	17.6	Background
10	19.2	Background
11	19.5	34.1 ppm Cd Added
12	19.2	Background
13	21.4	Background
14	19.2	38.5 ppm Cd Added
15	19.2	Background
16	21.4	71.0 ppm Cd Added
17	21.8	Background
18	22.7	Background
19	22.4	Background

TABLE 12

THE EFFECT OF LEAD ADDITIONS ON THE SUPERCOOLING BEHAVIOR OF BISMUTH

Freezing Cycle No.	Supercooling °C	Condition
1	34.2	Background
2	34.2	Background
3	34.2	Background
4	34.6	Background
5	31.0	11.0 ppm Pb Added
6	33.9	Background
7	32.6	Background
8	22.4	17.1 ppm Pb Added
9	23.0	Background
10	21.4	Background
11	21.8	33.8 ppm Pb Added
12	23.0	Background
13	19.2	50.1 ppm Pb Added
14	21.8	Background
15	23.0	Background

TABLE 13

THE EFFECT OF GOLD ADDITIONS ON THE SUPERCOOLING BEHAVIOR OF BISMUTH

Freezing Cycle No.	Supercooling °C	Condition
1	30.0	Background
2	27.8	Background
3	29.1	Background
4	26.2	Au in Melt
5	23.5	Background
6	22.7	Background
7	21.8	Au in Melt
8	22.4	Background
9	22.7	Au in Melt
10	24.0	Background

TABLE 14

THE EFFECT OF SILVER ADDITIONS ON THE SUPERCOOLING BEHAVIOR OF BISMUTH

Freezing Cycle No.	Supercooling °C	Condition
1	27.8	Background
2	29.8	Background
3	29.4	Background
4	29.1	Background
5	27.5	Ag in Melt
6	25.6	Background
7	23.0	Background
8	24.0	Background
9	23.7	Ag in Melt
10	22.4	Background

TABLE 15

THE EFFECT OF COPPER ADDITIONS ON THE SUPERCOOLING BEHAVIOR OF BISMUTH

Freezing Cycle No.	Supercooling °C	Condition
1	30.4	Background
2	28.5	Background
3	29.1	Cu in Melt
4	27.2	Background
5	27.2	Cu in Melt
6	25.6	Background
7	25.3	Background
8	24.6	Background
9	24.6	Background
10	24.6	Cu in Melt
11	21.4	Background

Some Thermodynamic Calculations of the Reduction of Bismuth Oxide

Thermodynamic Data at 600°K[52][53]

Compound	Heat of Formation Kcal/mole.	Free Energy of Formation Kcal/mole.
Bi_2O_3	-142	- 99
Sb_2O_3	-169	-130
In_2O_3	-220	-180*
CdO	- 62.5	- 41.8
PbO	- 51.6	- 37.9
H_2O	- 58.5	- 50.0

* Approximated

(a) Reduction by Hydrogen

Reaction: $Bi_2O_3 + 3H_2 \rightarrow 2Bi + 3H_2O$

$$\Delta F_r = 3(-50.0) - (-99.) = -51.0 \text{ Kcal}$$

(b) Reduction by Antimony

Reaction: $Bi_2O_3 + Sb \rightarrow Bi + Sb_2O_3$

$$\Delta F_r = (-130) - (-99) = -31 \text{ Kcal}$$

(c) Reduction by Indium

Reaction: $Bi_2O_3 + In \rightarrow Bi + In_2O_3$

$$\Delta F_r = (-180) - (-99) = -79 \text{ Kcal}$$

(d) <u>Reduction by Cadmium</u>

Reaction: $Bi_2O_3 + 3\ Cd \rightarrow 2\ Bi + 3\ CdO$

$$\Delta F_R = 3(-41.8) - (-99) = -126.4 \text{ Kcal}$$

(e) <u>Reduction by Lead</u>

Reaction: $Bi_2O_3 + 3\ Pb \rightarrow 2\ Bi + 3\ PbO$

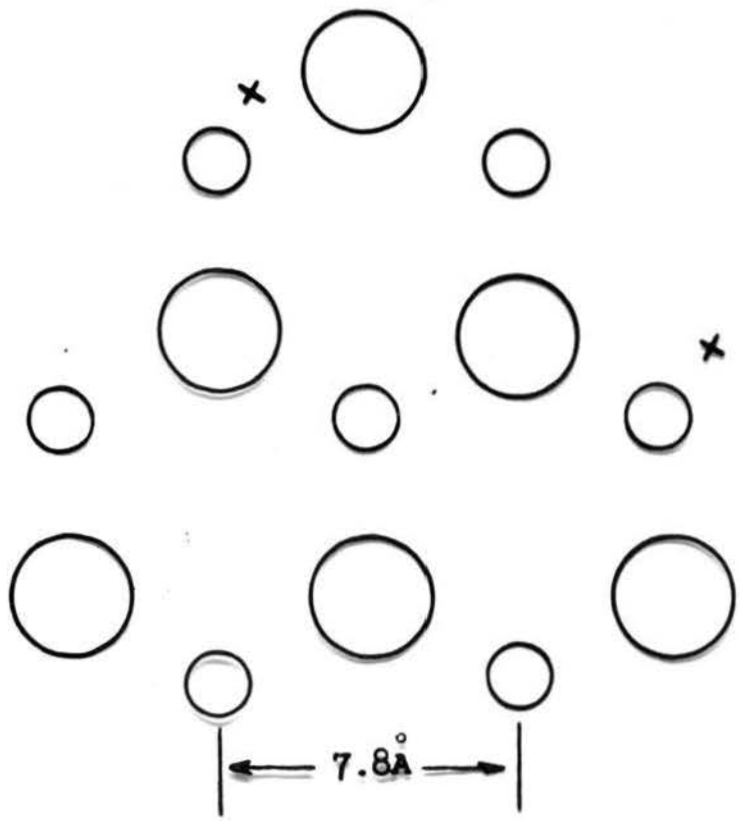
$$\Delta F_R = 3(-37.9) - (-99) = -114.7 \text{ Kcal.}$$

TRANSPARENCIES OF PROPOSED CRYSTALLOGRAPHIC PLANES OF THE SURFACE MONOLAYERS

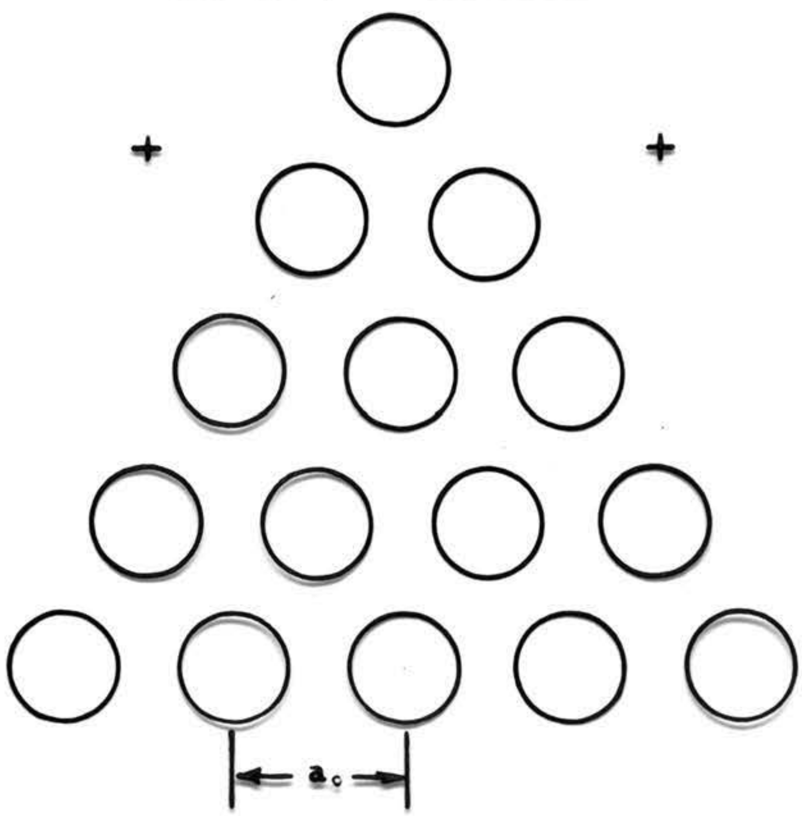
VITA

The author was born in Troy, New York on February 4, 1938. He received his primary and secondary education in the public schools in Watervliet, New York. A Bachelor of Science Degree in Metallurgical Engineering, Nuclear Engineering Option, was received from the University of Missouri School of Mines and Metallurgy in Rolla, Missouri on May 29, 1960. A Master of Science Degree in Metallurgical Engineering was received from the same University on May 27, 1962. In the fall of 1962, the author enrolled in the University of Missouri at Rolla for further study and since that time held the position of Instructor of Metallurgical Engineering.

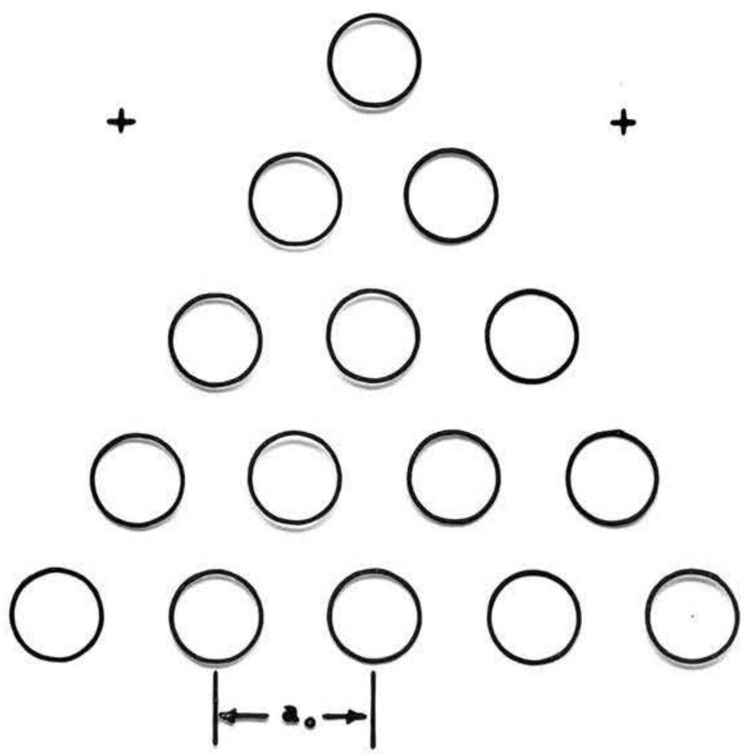
The (111) of Antimony Oxide, Sb_2O_3



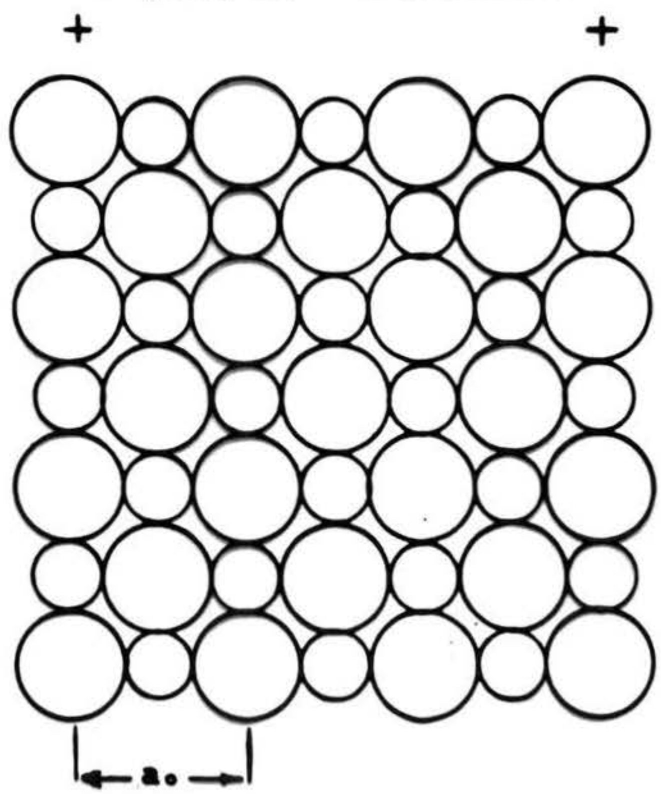
The (001) of Tellurium



The (001) of Selenium



The (001) of Cadmium Oxide



The (111) of Gold and Silver